

# Spectroscopic Properties of $\text{Al}_2\text{P}_2$ , $\text{Al}_2\text{P}_2^+$ , and $\text{Al}_2\text{P}_2^-$ and Comparison with Their Ga and In Analogues

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Sixteen electronic states of  $\text{Al}_2\text{P}_2$ , three states of  $\text{Al}_2\text{P}_2^+$ , and the ground state of  $\text{Al}_2\text{P}_2^-$  are studied using the complete active-space MCSCF (CASSCF) followed by multireference singles + doubles configuration interaction (MRSDCI). The  $^1\text{A}_g$ ,  $^2\text{B}_{1u}$ , and  $^2\text{B}_{1g}$  electronic states with rhombus equilibrium structures were found to be the ground states of  $\text{Al}_2\text{P}_2$ ,  $\text{Al}_2\text{P}_2^+$ , and  $\text{Al}_2\text{P}_2^-$ , respectively. Alternative structures such as T-shaped, linear, and trapezoidal structures were considered, but the equilibrium geometry of the ground state was found to be the rhombus structure. Our computed results are compared with anion photoelectron spectroscopic studies of Neumark and co-workers. Comparison of electronic states of  $\text{M}_2\text{P}_2$  ( $\text{M} = \text{Al}$ , Ga, and In) was made. It is shown that the electronic states of  $\text{In}_2\text{P}_2$  exhibit anomalies due to relativistic effects.

## 1. Introduction

The III–V semiconductor clusters have been the topic of many experimental and theoretical studies.<sup>1–20</sup> A primary driving force behind such studies is that the III–V materials are of great technological importance as they find applications in the fabrication of fast microelectronic devices, small devices, and light-emitting diodes. Consequently, a detailed study of the properties of such clusters as a function of their sizes could provide significant insight into the evolution from the molecular level to the bulk. Moreover, surface–molecular processes that take place between semiconductor surfaces and gas-phase molecules in their proximity, for example, in halogen etching of semiconductor materials, involve localized clusters of the III–V elements.

The advent of the supersonic jet expansion technique followed by laser vaporization of a III–V semiconductor foil has made it feasible to generate mixed III–V clusters of a variety of composition and isomers.<sup>1–13</sup> Thus, spectroscopy of the III–V semiconductor clusters with different compositions can be studied using a variety of techniques, and such studies have culminated into a wealth of information and spectroscopic data on these species.<sup>1–14</sup> An intriguing feature of these clusters is that they exhibit dramatic variation in abundance and properties as a function of their size, which is very baffling. Moreover, the isomers of III–V clusters of a given constitution exhibit dramatic variations in their properties. For example, Reents<sup>14</sup> had observed that certain isomers of gallium arsenide clusters react readily in halogen etching, while the others are somewhat inert. The existence of isomers for  $\text{Ga}_x\text{As}_y$  clusters was revealed by this work, which revealed that the reactivity of isomers contrasted dramatically in the reactive etching of  $\text{Ga}_x\text{As}_y^-$  with the halogen radicals. Consequently, systematic studies of these clusters for various sizes and compositions could provide significant insight into how their properties evolve as a function of their size.

In the supersonic jet expansion technique, a source material of the III–V compound such as a foil is laser-evaporated and passed through a supersonic nozzle, which results in cooling and formation of clusters of various sizes. The clusters can be mass analyzed, and a variety of spectroscopic techniques could then be utilized to investigate the low-lying electronic states of these clusters as a function of their size.

Neumark and co-workers<sup>1–5</sup> have studied a number of III–V semiconductor clusters employing anion photodetachment spectroscopic and zero electron kinetic energy spectroscopic techniques. The anion photoelectron spectroscopic technique is especially valuable to probe the electronic states to which optical spectroscopic transitions may be forbidden due to dipole selection rules. Although spectroscopic investigations of  $\text{Al}_x\text{P}_y$  clusters are yet to be made using these techniques, Neumark and co-workers<sup>4</sup> have studied the related indium phosphide clusters containing 2–8 atoms using anion photoelectron spectroscopy of  $\text{In}_x\text{P}_y^-$  ( $x, y = 1–4$ ). In another study Arnold and Neumark<sup>3</sup> have investigated the electronic states of trimeric clusters of the formulas  $\text{In}_2\text{P}$  and  $\text{InP}_2$  using the anion photodetachment spectroscopic method. These studies have provided valuable information on the electron affinities and the low-lying excited electronic states of these clusters as a function of cluster size.

Weltner and co-workers<sup>13</sup> have employed the matrix-isolation technique to trap the clusters of III–V compounds, which are subsequently investigated using the electron spin resonance (ESR) spectroscopic method to probe the ground states of the matrix-isolated clusters. The hyperfine patterns of the spectra have provided valuable information on the geometries and spin populations of the ground states of these species. In addition, the spin multiplicities and the probable ground electronic states of these species can be inferred from these spectra.

Although several theoretical studies have been made on  $\text{Ga}_x\text{As}_y$  and related III–V clusters,<sup>9,11,15–20</sup> there are relatively fewer studies of the aluminum phosphide clusters. The geometries and energy separations of the low-lying electronic states of gallium arsenide clusters<sup>9,11,16–19</sup> have been obtained for

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several smaller clusters. More recently, the authors<sup>19,20</sup> have studied clusters containing In and P. While the ground states of many of these clusters have been studied, it is important to obtain information on the excited electronic states, their geometries, and energy separations. Such studies that include excited electronic states are particularly valuable for the assignment of experimental spectra. Furthermore, theoretical studies of excited electronic states are challenging since electron correlation effects for the electronic states of different geometries and spin multiplicities are quite different. Likewise, anions of the clusters and the computation of the electron affinities have been quite difficult. To the best of the authors' knowledge, the low-lying electronic states of  $\text{Al}_2\text{P}_2$  and their ions have not been investigated at the level of theory considered here.

The above survey of experimental and theoretical studies of the III–V clusters indicates a compelling need for a theoretical study of the low-lying electronic states  $\text{Al}_2\text{P}_2$ ,  $\text{Al}_2\text{P}_2^+$ , and  $\text{Al}_2\text{P}_2^-$ . In this work we consider a systematic study on several low-lying electronic states of these species using ab initio CASSCF/MRSDCI techniques that included up to a million configurations and relativistic effects through relativistic effective core potentials. Both ground and several low-lying excited electronic states of these species are optimized, and their energy separations are computed.

## 2. Methods of Computation

All of the computations considered here for both the neutral and ionic species of  $\text{Al}_2\text{P}_2$  started with the complete active space self-consistent field (CASSCF) technique for the zeroth-order optimization of the orbitals in the full CI space of the valence orbitals. After this, higher-order MRSDCI (multireference singles + doubles configuration interaction) computations were carried out. We employed relativistic effective core potentials (RECPs) that retained the outer  $3s^23p^1$  and  $3s^23p^3$  shells of Al and P, respectively, in the valence space, replacing the rest of the electrons by RECPs. The RECPs together with valence Gaussian basis sets were taken from ref 21. The valence Gaussian basis sets from ref 21 were augmented with one set of d functions ( $\alpha_d = 0.3084$ ) for Al and two sets of d functions ( $\alpha_{d1} = 1.20$  and  $\alpha_{d2} = 0.3$ ) for P. In one of the authors' previous studies on the neutral  $\text{Ga}_2\text{As}_2$ , it was discovered that rhombus is the most favorable structure among the linear, trapezoidal, and rhombus isomers of  $\text{Ga}_2\text{As}_2$ . For the singlet electronic state the rhombus structure was not assumed as the equilibrium structure. We considered several possibilities such as a T-shaped structure in which P atoms are on the shorter side of the T, a  $\text{Al-P-P-Al}$  linear structure, and a trapezoidal structure. Full geometry optimization of all these different geometry arrangements was considered, and the rhombus structure was found to be the lowest for the ground state. The geometry optimization for all possible singlet and triplet excited electronic states of  $\text{Al}_2\text{P}_2$  was restricted to the rhombus structures. All final CASSCF and MRSDCI calculations were made in the  $D_{2h}$  group for the advantage of the molecular symmetry.

The quasi-Newton–Raphson geometry optimization procedure was invoked within the CASSCF level of theory. For this purpose, the GAMESS package<sup>23</sup> of molecular computational codes was employed. At the CASSCF level we kept two relatively low-lying 3s orbitals of P atoms inactive in that excitations were not allowed in the CASSCF calculations, although these orbitals were allowed to relax. However, excitations of electrons from these orbitals were allowed in the subsequent MRSDCI computations. The remaining orbitals

**TABLE 1: Geometries (Distances in Å and Angles in deg) and Energy Separations ( $E$ , in eV) for the Electronic States of  $\text{Al}_2\text{P}_2$ ,  $\text{Al}_2\text{P}_2^+$ , and  $\text{Al}_2\text{P}_2^-$  with Rhombus Geometries at the CASSCF Level**

system	state	Al–Al	P–P	Al–P	P–Al–P	$E$
$\text{Al}_2\text{P}_2$	$^1\text{A}_g$	4.600	2.123	2.533	49.5	0.00
	$^3\text{A}_u$	4.086	2.436	2.379	61.6	1.29
	$^1\text{A}_u$	4.084	2.432	2.377	61.5	1.34
	$^3\text{B}_{3u}$	3.188	3.366	2.318	93.1	1.45
	$^3\text{B}_{2g}$	4.729	2.161	2.600	49.1	1.55
	$^3\text{B}_{2u}$	4.577	2.439	2.593	56.1	1.96
	$^1\text{B}_{2g}$	4.734	2.170	2.604	49.3	2.02
	$^1\text{B}_{3u}$	3.194	3.387	2.328	93.4	2.02
	$^3\text{B}_{3g}$	3.793	3.032	2.428	77.3	2.88
	$^1\text{B}_{3g}$	3.786	3.062	2.435	77.9	3.02
	$^1\text{B}_{1g}$	4.107	2.481	2.399	62.3	3.15
	$^3\text{B}_{1g}$	4.116	2.496	2.407	62.5	3.24
	$^3\text{B}_{1u}$	3.731	3.331	2.501	83.5	3.48
	$^1\text{B}_{1u}$	3.747	3.466	2.552	85.5	4.10
	$^1\text{B}_{2u}$	4.039	2.543	2.386	64.4	4.29
$\text{Al}_2\text{P}_2^+$	$^3\text{A}_g$	4.612	2.188	2.552	50.8	4.48
	$^2\text{B}_{1u}$	4.584	2.100	2.521	49.2	7.04
	$^2\text{B}_{3g}$	4.584	2.100	2.521	49.2	7.19
$\text{Al}_2\text{P}_2^-$	$^2\text{B}_{3u}$	4.584	2.100	2.521	49.2	9.01
	$^2\text{B}_{1g}$	4.268	2.300	2.424	55.6	–0.57

spanned an active space comprising two  $a_g$ , one  $b_{2u}$ , two  $b_{1u}$ , one  $b_{3g}$ , two  $b_{3u}$ , one  $b_{1g}$ , and one  $b_{2g}$  orbital in the  $D_{2h}$  symmetric group.

The optimized geometries of all possible singlet and triplet electronic states for  $\text{Al}_2\text{P}_2$  in  $D_{2h}$  symmetry were further explored. Following CASSCF, the MRSDCI computations were carried out. The MRSDCI computations included all configurations in the CASSCF with coefficients  $\geq 0.07$  as reference configurations. Furthermore, the multireference Davidson corrections to the MRSDCI energy were calculated, and the resulting energy separations were labeled as MRSDCI + Q, which is considered to be full-CI estimates for correlation energies.

The electronic states of  $\text{Al}_2\text{P}_2^+$  positive and  $\text{Al}_2\text{P}_2^-$  negative ions were considered with the objective of not only computing the adiabatic ionization energies and electron affinity but also gaining information for possible photoionization studies of the neutral species. Three low-lying electronic states of  $\text{Al}_2\text{P}_2^+$  and the ground state of  $\text{Al}_2\text{P}_2^-$  were computed. To gain insight into the properties of the molecules, the atomization energies were computed. This was accomplished sequentially first by dissociating the  $\text{Al}_2\text{P}_2$  cluster into two aluminum atoms ( $^2\text{P}$ ) and the  $\text{P}_2$  molecule ( $^1\Sigma_g^+$ ) in their ground states. Subsequently, the  $\text{Al}_2\text{P}_2$  cluster was atomized into two aluminum atoms ( $^2\text{P}$ ) and two phosphorus atoms ( $^4\text{S}$ ). All of these dissociations were made as supermolecular computations.

The MCSCF/MRSDCI calculations were made using one of the authors' modified version of ALCHEMY II codes<sup>25</sup> to include relativistic ECPs (RECPs).

## 3. Results and Discussions

**Electronic States of  $\text{Al}_2\text{P}_2$ .** The equilibrium geometries and energy separations for all singlet and triplet electronic states of  $\text{Al}_2\text{P}_2$  in rhombus structures ( $D_{2h}$  symmetry) optimized at the CASSCF level are exhibited in Table 1. As seen from Table 1, a closed shell  $^1\text{A}_g$  state is unambiguously the ground state of  $\text{Al}_2\text{P}_2$  since the first excited  $^3\text{A}_u$  state is considerably higher than the ground state (1.29 eV). At the CASSCF level, the P–P diagonal bond length of the  $^1\text{A}_g$  state is 2.123 Å and is much shorter than the Al–Al bond length of 4.60 Å, resulting in an acute P–Al–P bond angle of 49.5° for the rhombus structure.

**TABLE 2: Geometries (Distances in Å and Angles in deg) and Energy Separations (*E*, in eV) for the Electronic States of Al<sub>2</sub>P<sub>2</sub>, Al<sub>2</sub>P<sub>2</sub><sup>+</sup>, and Al<sub>2</sub>P<sub>2</sub><sup>-</sup> in Rhombus Structures at the MRSDCI Level**

system	state	Al–Al	P–P	Al–P	P–Al–P	<i>E</i> <sup>a</sup>
Al <sub>2</sub> P <sub>2</sub>	<sup>1</sup> A <sub>g</sub>	4.584	2.100	2.521	49.2	0.00 (0.00)
	<sup>3</sup> A <sub>u</sub>	4.105	2.356	2.367	59.7	1.12 (0.86)
	<sup>1</sup> A <sub>u</sub>	4.089	2.370	2.362	60.1	1.22 (1.00)
	<sup>3</sup> B <sub>3u</sub>	3.179	3.333	2.303	92.7	1.41 (1.12)
	<sup>3</sup> B <sub>2g</sub>	4.695	2.130	2.578	48.8	1.50 (1.40)
	<sup>1</sup> B <sub>3u</sub>	3.168	3.350	2.305	93.2	1.93 (1.64)
	<sup>1</sup> B <sub>2g</sub>	4.706	2.125	2.582	48.6	2.08 (2.02)
	<sup>3</sup> B <sub>2u</sub>	4.588	2.367	2.581	54.6	2.24 (2.27)
	<sup>3</sup> B <sub>3g</sub>	3.804	2.934	2.402	75.3	2.65 (2.27)
	<sup>1</sup> B <sub>3g</sub>	3.804	2.892	2.389	74.5	2.81 (2.41)
	<sup>1</sup> B <sub>1g</sub>	4.083	2.388	2.365	60.6	3.03 (2.79)
	<sup>3</sup> B <sub>1g</sub>	4.069	2.371	2.355	60.5	3.09 (2.84)
	<sup>3</sup> B <sub>1u</sub>	3.746	3.200	2.463	81.0	3.30 (2.93)
	<sup>1</sup> B <sub>1u</sub>	3.755	3.222	2.474	81.3	3.99 (3.60)
	<sup>1</sup> B <sub>2u</sub>	4.078	2.444	2.377	61.9	4.18 (3.75)
	<sup>3</sup> A <sub>g</sub>	4.593	2.131	2.532	49.8	4.76 (4.55)
2Al( <sup>2</sup> P) + P <sub>2</sub> ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )						3.87 (3.89)
2Al( <sup>2</sup> P) + 2P( <sup>4</sup> S)						8.90 (8.92)
Al <sub>2</sub> P <sub>2</sub> <sup>+</sup>	<sup>2</sup> B <sub>1u</sub>	4.584	2.100	2.521	49.2	7.38 (7.20)
	<sup>2</sup> B <sub>3g</sub>	4.584	2.100	2.521	49.2	7.84 (7.76)
	<sup>2</sup> B <sub>3u</sub>	4.584	2.100	2.521	49.2	9.35 (9.04)
Al <sub>2</sub> P <sub>2</sub> <sup>-</sup>	<sup>2</sup> B <sub>1g</sub>	4.282	2.242	2.417	55.3	-1.09 (-1.33)

<sup>a</sup> The values in the parentheses are the Davidson corrected energies.

The P–P bond length in the <sup>1</sup>A<sub>g</sub> state of Al<sub>2</sub>P<sub>2</sub> at the CASSCF level is longer than the corresponding bond length of the <sup>1</sup>Σ<sub>g</sub><sup>+</sup> ground state of P<sub>2</sub>, which is 1.8934 Å.<sup>26</sup> This suggests that the P–P diagonal interaction in Al<sub>2</sub>P<sub>2</sub> is weaker than a triple bond in P<sub>2</sub> as expected due to the presence of the Al–P bonds along the four equal sides of the rhombus. The Al–Al bond length in the <sup>1</sup>A<sub>g</sub> state of Al<sub>2</sub>P<sub>2</sub> is 4.600 Å. Since the Al–Al bond length in the <sup>2</sup>A<sub>1</sub> ground state of Al<sub>3</sub> is 2.521 Å at the CASSCF level,<sup>27</sup> the Al–Al bonding in Al<sub>2</sub>P<sub>2</sub> is dramatically weakened by the presence of the P–P and Al–P bonds. It is thus concluded that the P–P bonding plays a more important role in the determination of the geometries and energy separations for the electronic states of Al<sub>2</sub>P<sub>2</sub>.

For the singlet ground electronic state, other geometries were considered, as noted before. Among the various geometries considered, a T-shaped structure was found to be 0.73 eV above the rhombus structure. The T-shaped structure contains a P–P bond in a horizontal orientation with a bond length of 2.315 Å, while the closet Al–P bond distances are 2.918 Å, and the Al–Al distance is 2.777 Å. In the Al–P–P–Al linear structure the Al–P and P–P distances are 2.346 and 2.016 Å, respectively. The linear structure was found to be 2.41 eV above the rhombus structure.

Table 2 shows the equilibrium geometries and energy separations of the electronic states of Al<sub>2</sub>P<sub>2</sub> at the MRSDCI level, which contains more accurate results as the MRSDCI technique includes higher-order electron correlation effects. From the results of the CASSCF and MRSDCI results in Tables 1 and 2, it is seen that for most low-lying electronic states higher-order electron correlation effects do not substantially alter the geometries. A noticeable geometrical change is that all of the bond lengths (Al–Al, P–P, and Al–P) of the electronic states decrease slightly at the MRSDCI level compared to the CASSCF level, resulting in more acute P–Al–P bond angles. For example, the P–Al–P bond angles are 49.2°, 59.7°, and 60.1° for the <sup>1</sup>A<sub>g</sub>, <sup>3</sup>A<sub>u</sub>, and <sup>1</sup>A<sub>u</sub> states, respectively, at the

MRSDCI level compared to 49.5°, 61.6°, and 61.5° for the corresponding states at the CASSCF level.

The electron correlation effects have substantially greater impact on the relative energy separations of the low-lying electronic states at the MRSDCI level. For example, it is seen that the <sup>3</sup>A<sub>u</sub> and <sup>1</sup>A<sub>u</sub> states are 1.29 and 1.34 eV higher than the <sup>1</sup>A<sub>g</sub> ground state at the CASSCF level, while these values are decreased to 0.86 and 1.00 eV at the MRSDCI level.

Although the rhombus structure is the most stable geometry for the ground state of Al<sub>2</sub>P<sub>2</sub>, it may not be true for all of the excited states listed in Tables 1 and 2, since the optimization for the geometries of the excited states was restricted to the *D*<sub>2h</sub> symmetry. In particular, a T structure may be feasible for some higher-lying excited states of Al<sub>2</sub>P<sub>2</sub>. However, the energy separations of the excited states would not be influenced too much by such geometrical changes. It is expected that such geometrical changes may not induce more than 10% change to energy separations listed in Table 2. Furthermore, Franck–Condon type electronic excitations from the rhombus ground state would end up in local rhombus excited minima.

The dipole-allowed electronic transitions from the <sup>1</sup>A<sub>g</sub> ground state are to the <sup>1</sup>B<sub>1u</sub>, <sup>1</sup>B<sub>2u</sub>, and <sup>1</sup>B<sub>3u</sub> excited states. As seen from Table 2, these states lie at 1.93 (<sup>1</sup>B<sub>3u</sub>), 3.99 (<sup>1</sup>B<sub>1u</sub>), and 4.18 eV (<sup>1</sup>B<sub>2u</sub>) at the MRSDCI level and 1.64, 3.60, and 3.75 eV, respectively, at the MRSDCI + Q level. Among these, the transition to the <sup>1</sup>B<sub>3u</sub> electronic state is more likely to be observed in spectroscopic techniques such as anion photoionization spectroscopy since the energy of the transition is not too high. In the next section we shall predict the photoionization spectra of Al<sub>2</sub>P<sub>2</sub><sup>-</sup> and compare them with the corresponding spectra reported by Neumark and co-workers<sup>4</sup> for In<sub>2</sub>P<sub>2</sub><sup>-</sup>.

The atomization energy for Al<sub>2</sub>P<sub>2</sub> was computed sequentially as a supermolecular computation. As seen from Table 2, the energy required to break the Al–P bonds in the Al<sub>2</sub>P<sub>2</sub> cluster resulting in two Al atoms (<sup>2</sup>P) and the P<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) dimer is 3.87 eV at the MRSDCI level. The fact that the MRSDCI + Q level is only 0.02 eV higher than the MRSDCI result suggests that the MRSDCI computation is quite complete and is close to the full CI estimate. The atomization energy to fully separate Al<sub>2</sub>P<sub>2</sub> into two Al(<sup>2</sup>P) and two phosphorus atoms (<sup>4</sup>S) is calculated to be 8.90 and 8.92 eV at MRSDCI and MRSDCI + Q levels, respectively. This is consistent with our anticipation that the P–P bonding is considerably stronger than that of the Al–Al bond in Al<sub>2</sub>P<sub>2</sub> and plays a more important role in the properties for the electronic states of Al<sub>2</sub>P<sub>2</sub>.

Next we consider the nature of the low-lying electronic states of the neutral species. Table 3 shows the Mulliken population distributions, which suggest that all of the electronic states in Al<sub>2</sub>P<sub>2</sub> exhibit charge transfers from Al to P resulting in Al<sup>+</sup>P<sup>-</sup> ionic bonds. The d populations of P are considerably larger than the corresponding d populations on Al due to the participation of the 3d polarization functions. All of the electronic states exhibit reduced s populations compared to atomic populations, consistent with anticipated hybridization with the 3p orbitals. The P(3p) populations in all of the electronic states of Al<sub>2</sub>P<sub>2</sub> are uniformly larger than 3, which suggests that most of the charge transferred from the Al atoms is received by the P(3p) orbitals. In comparing the ground-state populations with the low-lying excited electronic states' populations, it is seen that the excited states exhibit larger Al(3p) populations and smaller Al(3s) populations, suggesting 3s to 3p promotions on Al in the excited states. This results in the enhancement of the Al–P bonding as seen from the larger Al–P overlap populations and decrease in the P–P bonding in the excited electronic states.



**TABLE 3: Mulliken Population Analysis for the Low-Lying Electronic States of  $\text{Al}_2\text{P}_2$ ,  $\text{Al}_2\text{P}_2^+$ , and  $\text{Al}_2\text{P}_2^-$** 

system	state ( $D_{2h}$ )	total		gross population						overlap Al-P
		Al	P	Al (s)	Al (p)	Al (d)	P (s)	P (p)	P (d)	
$\text{Al}_2\text{P}_2$	$^1\text{A}_g$	2.676	5.324	1.829	0.754	0.093	1.820	3.336	0.169	0.274
	$^3\text{A}_u$	2.634	5.366	1.595	0.923	0.117	1.810	3.413	0.143	0.710
	$^1\text{A}_u$	2.643	5.357	1.570	0.955	0.118	1.808	3.405	0.144	0.733
	$^3\text{B}_{3u}$	2.680	5.320	1.389	1.162	0.129	1.795	3.415	0.111	1.687
	$^3\text{B}_{2g}$	2.590	5.410	1.834	0.672	0.084	1.836	3.409	0.166	0.242
	$^1\text{B}_{3u}$	2.663	5.337	1.392	1.141	0.131	1.799	3.428	0.111	1.184
	$^1\text{B}_{2g}$	2.598	5.402	1.842	0.673	0.084	1.835	3.402	0.166	0.243
	$^3\text{B}_{2u}$	2.633	5.367	1.825	0.722	0.087	1.868	3.367	0.132	0.207
	$^3\text{B}_{3g}$	2.674	5.326	1.621	0.941	0.113	1.841	3.373	0.113	0.555
	$^1\text{B}_{3g}$	2.679	5.321	1.591	0.974	0.114	1.835	3.371	0.116	0.599
	$^1\text{B}_{1g}$	2.647	5.353	1.377	1.151	0.120	1.812	3.405	0.136	0.760
	$^3\text{B}_{1g}$	2.639	5.361	1.376	1.140	0.124	1.804	3.419	0.139	0.790
	$^3\text{B}_{1u}$	2.604	5.396	1.628	0.873	0.104	1.863	3.432	0.102	0.463
	$^1\text{B}_{1u}$	2.602	5.398	1.662	0.838	0.103	1.866	3.431	0.102	0.404
	$^1\text{B}_{2u}$	2.607	5.393	1.466	1.023	0.119	1.791	3.441	0.162	0.657
	$^3\text{A}_g$	2.634	5.366	1.477	1.066	0.092	1.820	3.379	0.167	0.255
$\text{Al}_2\text{P}_2^+$	$^2\text{B}_{1u}$	2.309	5.191	1.619	0.606	0.084	1.835	3.188	0.169	
	$^2\text{B}_{3g}$	2.464	5.036	1.884	0.493	0.087	1.838	3.022	0.176	
	$^2\text{B}_{3u}$	2.258	5.242	1.631	0.545	0.082	1.839	3.230	0.174	
$\text{Al}_2\text{P}_2^-$	$^2\text{B}_{1g}$	2.970	5.530	1.751	1.106	0.114	1.799	3.579	0.152	

**TABLE 4: Leading Configurations for the Low-Lying Electronic States of  $\text{Al}_2\text{P}_2$ ,  $\text{Al}_2\text{P}_2^+$ , and  $\text{Al}_2\text{P}_2^-$** 

system	state ( $D_{2h}$ )	coeff	configurations												
			$1a_g$	$2a_g$	$3a_g$	$1b_{2u}$	$2b_{2u}$	$1b_{1u}$	$2b_{1u}$	$1b_{3g}$	$1b_{3u}$	$2b_{3u}$	$1b_{1g}$	$1b_{2g}$	$1a_u$
$\text{Al}_2\text{P}_2$	$^1\text{A}_g$	0.881	2	2	2	2	0	2	2	2	2	0	0	0	0
	$^3\text{A}_u$	0.885	2	2	2	2	0	2	1	2	2	0	1	0	0
	$^1\text{A}_u$	0.872	2	2	2	2	0	2	1	2	2	0	1	0	0
	$^3\text{B}_{3u}$	0.808	2	2	2	2	1	2	0	2	2	0	1	0	0
	$^3\text{B}_{2g}$	0.889	2	2	2	2	0	2	2	1	2	0	1	0	0
	$^1\text{B}_{3u}$	0.804	2	2	2	2	1	2	0	2	2	0	1	0	0
	$^1\text{B}_{2g}$	0.887	2	2	2	2	0	2	2	1	2	0	1	0	0
	$^3\text{B}_{2u}$	0.897	2	2	2	2	0	2	2	2	1	0	1	0	0
	$^3\text{B}_{3g}$	0.839	2	2	2	2	1	2	1	2	2	0	0	0	0
	$^1\text{B}_{3g}$	0.837	2	2	2	2	1	2	1	2	2	0	0	0	0
	$^1\text{B}_{1g}$	0.782	2	2	1	2	0	2	2	2	2	0	1	0	0
	$^3\text{B}_{1g}$	0.803	2	2	1	2	0	2	2	2	2	0	1	0	0
	$^3\text{B}_{1u}$	0.851	2	2	2	2	1	2	1	2	1	0	1	0	0
	$^1\text{B}_{1u}$	0.850	2	2	2	2	1	2	1	2	1	0	1	0	0
	$^1\text{B}_{2u}$	0.669	2	2	2	2	0	2	0	2	2	1	1	0	0
		0.416	2	2	2	2	0	2	1	1	2	0	2	0	0
	$^3\text{A}_g$	0.660	2	2	2	2	0	2	1	1	2	1	1	0	0
		0.480	2	2	1	2	0	2	2	1	2	0	1	1	0
$\text{Al}_2\text{P}_2^+$	$^2\text{B}_{1u}$	0.891	2	2	2	2	0	2	1	2	2	0	0	0	0
	$^2\text{B}_{3g}$	0.877	2	2	2	2	0	2	2	1	2	0	0	0	0
	$^2\text{B}_{3u}$	0.819	2	2	2	2	0	2	2	2	1	0	0	0	0
$\text{Al}_2\text{P}_2^-$	$^2\text{B}_{1g}$	0.883	2	2	2	2	0	2	2	2	2	0	1	0	0

Table 4 shows the leading electronic configurations for the electronic states of  $\text{Al}_2\text{P}_2$ . The coefficients of the leading configurations for all the electronic states are smaller than 0.9, indicating the significance of electron correlation effects. As seen from Table 4, the  $1a_g^2 2a_g^2 1b_{2u}^2 1b_{1u}^2$  portion of the electronic configuration is common for all of the electronic states of  $\text{Al}_2\text{P}_2$ . The differences in the properties among the electronic states arise from the occupancies for the  $3a_g$ ,  $2b_{2u}$ ,  $2b_{1u}$ ,  $1b_{3g}$ ,  $1b_{3u}$ ,  $2b_{3u}$ ,  $1b_{1g}$ , and  $1b_{2g}$  orbitals. Consequently, analysis of the compositions of these orbitals could provide insight into the nature of the low-lying electronic states. The  $3a_g$  bonding orbital is composed of  $[\text{Al}_1(s) + \text{Al}_2(s)] - [\text{P}_1(s) + \text{P}_2(s)]$ , and it is more localized orbital between the P atoms (and Al atoms). The  $2b_{2u}$  orbital is made of  $[\text{P}_1(p_y) + \text{P}_2(p_y)]$ , and it is an antibonding  $\sigma$  orbital, since the two  $P_y$  lobes on the phosphorus atoms mix with opposite signs along the y axis. The  $2b_{1u}$  orbital is mainly on  $[\text{Al}_1(s) - \text{Al}_2(s)]$  combined with  $[\text{Al}_1(p_z) + \text{Al}_2(p_z)] - [\text{P}_1(p_z) + \text{P}_2(p_z)]$ . Thus, the first part represents a repulsive interaction between two aluminum atoms, but the second part is a bonding  $\pi$  interaction between two phosphorus

atoms. The  $1b_{3g}$  orbital is  $[\text{P}_1(p_z) - \text{P}_2(p_z)]$ , which is an antibonding  $\pi$  orbital in which two phosphorus atoms furnish P orbitals overlapping with opposite lobes along the z axis. The  $1b_{3u}$  and the  $2b_{3u}$  orbitals are bonding  $\pi$  orbitals composed of  $[\text{P}_1(p_x) + \text{P}_2(p_x)]$  and  $[\text{Al}_1(p_x) + \text{Al}_2(p_x)]$ , respectively. The  $1b_{1g}$  antibonding  $\pi$  orbital is made of  $[\text{P}_1(p_x) - \text{P}_2(p_x)]$ , while the  $1b_{2g}$  orbital is  $[\text{Al}_1(p_x) + \text{Al}_2(p_x)]$ , and it is a bonding  $\pi$  orbital between two aluminum atoms.

In the  $^1\text{A}_g$  ground state, the  $3a_g$ ,  $2b_{1u}$ ,  $1b_{3g}$ , and  $1b_{3u}$  orbitals are doubly occupied, and these orbitals exhibit strong bonding interaction between the phosphorus atoms. Consequently, the ground state has a much shorter P-P diagonal, resulting in the rhombus equilibrium structure. All the excited states arise from transfer of electrons from the bonding to the antibonding orbitals, resulting in energies above the  $^1\text{A}_g$  ground state of  $\text{Al}_2\text{P}_2$ . For example, the differences in the properties of the  $^1\text{A}_g$  ground state and the  $^3\text{A}_u$  first excited state arise as a consequence of the occupancies for the  $2b_{1u}$  and  $1b_{1g}$  orbitals. The  $2b_{1u}$  orbital which contains strong  $\pi$  bonding between two P atoms is fully occupied in  $^1\text{A}_g$  but half-filled in  $^3\text{A}_u$ , while

the 1b<sub>1g</sub> antibonding  $\pi$  orbital between the P atoms is singly occupied in <sup>3</sup>A<sub>u</sub>.

The nature of the orbitals facilitates rationalization of the Mulliken populations. As seen from the Table 3, the gross Al(s) population of the <sup>1</sup>A<sub>g</sub> state is 1.829, which is larger than the relevant value of 1.595 for <sup>3</sup>A<sub>u</sub>. On the contrary, the gross P(p) population for the <sup>1</sup>A<sub>g</sub> (3.336) is smaller than the corresponding value for <sup>3</sup>A<sub>u</sub> (3.413). This is a consequence of the fact that the Al(s) is the main part of the 2b<sub>1u</sub> orbital, while the 1b<sub>1g</sub> orbital is composed mainly of P(p).

**The Electronic States of Al<sub>2</sub>P<sub>2</sub><sup>+</sup> and Al<sub>2</sub>P<sub>2</sub><sup>-</sup> and Predictions of Photoionization Spectra of Al<sub>2</sub>P<sub>2</sub><sup>-</sup>.** An important property of a cluster is the first ionization energy of the cluster. The vertical ionization energies of Al<sub>2</sub>P<sub>2</sub> to three possible low-lying states of Al<sub>2</sub>P<sub>2</sub><sup>+</sup> were calculated at both CASSCF and MRSDCI levels of theory, as illustrated in Tables 1 and 2. On the basis of the leading configurations presented in Table 3, we expect three highest-occupied orbitals to be close to each other, and thus removal of an electron from each of those orbitals would lead to the <sup>2</sup>B<sub>1u</sub>, <sup>2</sup>B<sub>3g</sub>, and <sup>2</sup>B<sub>3u</sub> states for the positive ion. Removal of an electron from the 2b<sub>1u</sub> HOMO of the <sup>1</sup>A<sub>g</sub> state leads to the <sup>2</sup>B<sub>1u</sub> state, which is the ground state of Al<sub>2</sub>P<sub>2</sub><sup>+</sup>. Thus, the vertical ionization energy of Al<sub>2</sub>P<sub>2</sub> to yield the <sup>2</sup>B<sub>1u</sub> state is computed as 7.04 and 7.38 eV at the CASSCF and MRSDCI levels, respectively. The first excited state of the Al<sub>2</sub>P<sub>2</sub><sup>+</sup> ion is <sup>2</sup>B<sub>3g</sub>, which is formed from the neutral <sup>1</sup>A<sub>g</sub> state by the removal of an electron from the 1b<sub>3g</sub> orbital, and the vertical ionization energy needed is 7.19 eV at the MRSDCI level. Consequently, the <sup>2</sup>B<sub>3g</sub> state is only 0.46 eV above the ground state at the MRSDCI level. The vertical ionization energy required to eject an electron from the 1b<sub>3u</sub> orbital in <sup>1</sup>A<sub>g</sub> is 9.35 eV (at the MRSDCI level), which is considerably higher resulting in the <sup>2</sup>B<sub>3u</sub> state of Al<sub>2</sub>P<sub>2</sub><sup>+</sup>. From the Mulliken population comparison between the <sup>1</sup>A<sub>g</sub> and <sup>2</sup>B<sub>1u</sub> states, it is seen that in the <sup>2</sup>B<sub>1u</sub> state of Al<sub>2</sub>P<sub>2</sub><sup>+</sup> there is a clear depletion of the 3s population on Al atoms after the ionization process. This is fully consistent with the nature of the 2b<sub>1u</sub> orbital, since the orbital is primarily composed of Al(3s). In the <sup>1</sup>A<sub>g</sub> state, the 2b<sub>1u</sub> orbital is fully occupied. Since an electron is removed from 2b<sub>1u</sub> after ionization, the Al(3s) population is decreased analogous to the <sup>2</sup>B<sub>1u</sub> state of Al<sub>2</sub>P<sub>2</sub><sup>+</sup>. Since the 1b<sub>3g</sub> orbital is mainly made of P(3p<sub>z</sub>) and the <sup>1</sup>A<sub>g</sub> state has full occupancy for the 1b<sub>3g</sub> orbital, removal of an electron from 1b<sub>3g</sub> results in a decrease of the P(3p) population in the <sup>2</sup>B<sub>3g</sub> state of Al<sub>2</sub>P<sub>2</sub><sup>+</sup>.

Next we consider the Al<sub>2</sub>P<sub>2</sub><sup>-</sup> anion and predictions of the anion photodetachment spectra of Al<sub>2</sub>P<sub>2</sub><sup>-</sup>. The ground electronic state of the anion was computed to be a <sup>2</sup>B<sub>1g</sub> state. The equilibrium geometry and the adiabatic electron affinity (EA) of the <sup>2</sup>B<sub>1g</sub> state are listed in Tables 1 and 2 at the CASSCF and MRSDCI levels, respectively. As shown in the tables, the Al–Al bond lengths of <sup>2</sup>B<sub>1g</sub> are 4.268 and 4.282 Å at the CASSCF and MRSDCI levels, respectively, which are 0.332 and 0.302 Å contracted compared to the corresponding Al–Al bond lengths of the <sup>1</sup>A<sub>g</sub> ground state of the neutral Al<sub>2</sub>P<sub>2</sub> at the same levels. The Al–P bond lengths of the <sup>2</sup>B<sub>1g</sub> state also shrink a bit, while the P–P bond length is a bit elongated in comparison to the corresponding bond lengths of the <sup>1</sup>A<sub>g</sub> state of Al<sub>2</sub>P<sub>2</sub>. This can be rationalized on the basis of the principal configurations, the composition of the orbitals, and the Mulliken populations exhibited in Tables 3 and 4. The Al<sub>2</sub>P<sub>2</sub><sup>-</sup> anion is formed by adding an electron to the 1b<sub>1g</sub> LUMO of the <sup>1</sup>A<sub>g</sub> state of the neutral Al<sub>2</sub>P<sub>2</sub>, resulting in the <sup>2</sup>B<sub>1g</sub> state of Al<sub>2</sub>P<sub>2</sub><sup>-</sup>. As shown before, the 1b<sub>1g</sub> orbital is composed of P<sub>1</sub>(p<sub>x</sub>) – P<sub>2</sub>(p<sub>x</sub>), which

is an antibonding  $\pi$  orbital between two phosphorus atoms. Therefore, the P–P interaction is weakened, while the Al–Al and Al–P interactions are enhanced during the formation of the Al<sub>2</sub>P<sub>2</sub><sup>-</sup> anion. The Mulliken population analysis reveals that the s populations on Al and P atoms in the <sup>2</sup>B<sub>1g</sub> state of Al<sub>2</sub>P<sub>2</sub><sup>-</sup> are smaller, while the p populations on these two atoms are larger compared to the corresponding populations of the <sup>1</sup>A<sub>g</sub> state of neutral Al<sub>2</sub>P<sub>2</sub>, consistent with the composition of the LUMO which is primarily composed of the 3p orbitals of Al and P atoms. The adiabatic electron affinity of (Al<sub>2</sub>P<sub>2</sub>) is computed as 1.09 and 1.33 eV, at the MRSDCI and MRSDCI + Q levels, respectively. We expect the MRSDCI + Q level to be the most accurate value for the adiabatic EA. Note that the CASSCF method computes the adiabatic EA as only 0.57, indicating the dramatic importance of electron correlation effects in computing the adiabatic EAs.

As mentioned before, Neumark and co-workers<sup>1–5</sup> have studied several III–V clusters using anion photoelectron spectroscopy. From these spectra, the adiabatic electron affinities and the energy separations of the low-lying electronic states of the neutral cluster can be determined. It appears that such spectroscopic studies on Al<sub>2</sub>P<sub>2</sub> have not been made up to now. Thus, our predictions would be interesting. We also compare our predictions with the anion photoelectron spectra of the analogous clusters. Xu et al.<sup>4</sup> have obtained the anion photoelectron spectra of In<sub>x</sub>P<sub>y</sub><sup>-</sup> for x, y = 1–4. It is therefore of interest to compare our computational results with the analogous In<sub>2</sub>P<sub>2</sub> observed by Xu et al.<sup>4</sup> The PES spectra of In<sub>2</sub>P<sub>2</sub><sup>-</sup> exhibit three distinct peaks labeled X, A, and B, where X corresponds to the ground state of In<sub>2</sub>P<sub>2</sub> and the A and B states are excited states of the neutral In<sub>2</sub>P<sub>2</sub>. From the spacing of the B and X peaks relative to the central A peak, it was inferred that the A and B states of the neutral In<sub>2</sub>P<sub>2</sub> are 1.2 and 2.0 eV above the X ground state, respectively. Our previous study on In<sub>2</sub>P<sub>2</sub><sup>20</sup> revealed that the <sup>3</sup>B<sub>2g</sub> excited state of In<sub>2</sub>P<sub>2</sub> lies 1.26 eV above the <sup>1</sup>A<sub>g</sub> ground state. There are three electronic states near the 1.6 eV region, namely, <sup>3</sup>A<sub>u</sub>, <sup>1</sup>A<sub>u</sub>, and <sup>1</sup>B<sub>2g</sub> states. The current authors thus assigned the A peak of the photoelectron spectrum of In<sub>2</sub>P<sub>2</sub><sup>-</sup> of Xu et al. to the <sup>3</sup>B<sub>2g</sub> excited state of In<sub>2</sub>P<sub>2</sub>. However, unambiguous assignment of the observed B state could not be made due to the existence of the <sup>3</sup>B<sub>2u</sub> and <sup>3</sup>B<sub>1u</sub> states computed at 1.90 and 2.17 eV.

On the basis of our computed results, we predict the following features in the anion photoelectron spectra of Al<sub>2</sub>P<sub>2</sub><sup>-</sup>. The lowest energy peak for the neutral Al<sub>2</sub>P<sub>2</sub>, which would correspond to the X ground state, should appear near 1.3 eV, which is deduced from our MRSDCI + Q electron affinity. Our computed energy separations of the excited electronic states of the neutral Al<sub>2</sub>P<sub>2</sub> are likely to be more accurate than the electron affinity of Al<sub>2</sub>P<sub>2</sub>. As seen from Table 2, the excited electronic states of Al<sub>2</sub>P<sub>2</sub> are considerably more clustered and complex compared to those of In<sub>2</sub>P<sub>2</sub>. This would result in several overlapping bands in the anion photoelectron spectra. The lowest excited <sup>3</sup>A<sub>u</sub> electronic state is 0.86 eV higher than the ground state, and this should correspond to the A peak in the spectrum. However, note that the <sup>1</sup>A<sub>u</sub> and <sup>3</sup>B<sub>3u</sub> states are 1.00 and 1.12 eV higher than the <sup>1</sup>A<sub>g</sub> ground state, and thus there is significant crowding in the 1 eV region. These bands are expected to overlap, and higher resolution may be warranted to resolve these peaks. The <sup>3</sup>B<sub>2g</sub> and <sup>1</sup>B<sub>3u</sub> excited states are 1.40 and 1.64 eV higher than the <sup>1</sup>A<sub>g</sub> ground state, and thus the two states are expected to be quite close, perhaps resulting in a coalesced peak. Again there are many electronic states in the 2 eV region which correspond to the B peak of In<sub>2</sub>P<sub>2</sub>. Overall, we expect the anion spectra of

**TABLE 5: Comparison of the Geometries (Distances in Å and Angles in deg) and Energy Separations ( $E$ , in eV) for the Electronic States of the  $M_2P_2$  (Rhombus Structures) at MRSDCI Level ( $M = Al, Ga, In$ )**

system	state	M–M	P–P	M–P	P–M–P	$E$
$Al_2P_2$	$^1A_g$	4.584	2.100	2.521	49.2	0.00
	$^3A_u$	4.105	2.356	3.367	59.7	0.86
	$^1A_u$	4.089	2.370	2.362	60.1	1.00
	$^3B_{3u}$	3.179	3.333	3.303	92.7	1.12
	$^3B_{2g}$	4.695	2.130	2.578	48.8	1.40
$Ga_2P_2$	$^1A_g$	4.690	2.100	2.569	48.2	0.00
	$^3A_u$	4.152	2.392	2.396	59.9	1.18
	$^1A_u$	4.124	2.474	2.405	61.9	1.38
	$^3B_{2g}$	4.790	2.123	2.620	47.8	1.53
	$^1B_{2g}$	4.804	2.140	2.630	48.0	1.79
$In_2P_2$	$^1A_g$	5.060	2.100	2.739	45.1	0.00
	$^3B_{2g}$	5.154	2.130	2.788	44.9	1.26
	$^3A_u$	4.526	2.458	2.575	57.0	1.58
	$^1A_u$	4.500	2.466	2.566	57.4	1.65
	$^1B_{2g}$	5.162	2.130	2.792	48.8	1.66

$Al_2P_2^-$  to be more crowded with a given coalesced peak possibly arising from more than one electronic state.

**Comparison of Electronic States of  $M_2P_2$  ( $M = Al, Ga$ , and  $In$ ).** The analogous III–V tetramers, namely,  $Ga_2P_2$  and  $In_2P_2$ , were studied by the authors before.<sup>19,20</sup> It is thus of interest to compare the electronic states of  $Al_2P_2$  with its heavier analogues. Table 5 lists the geometries and energy separations for some low-lying electronic states of these clusters at the same MRSDCI level of theory. Although there are many similarities among these three clusters, the  $Al_2P_2$  tetramer differs in some ways from the heavier analogues. As seen from Table 5, all three species have closed-shell  $^1A_g$  ground states with rhombus structures with exactly the same P–P bond lengths in the ground states. For all of the electronic states of  $M_2P_2$  with the rhombus structures in Table 5, the M–M distance is generally the longer diagonal, while the P–P distance is the shorter diagonal of the rhombus, leading to acute P–M–P bond angles.

It is expected that the M–M bond length would be longer within a group as the atomic number increases. Consequently, the Al–Al bond length in the  $^1A_g$  state of  $Al_2P_2$  is 4.584 Å, while the corresponding Ga–Ga and In–In bond lengths in the ground states of  $Ga_2P_2$  and  $In_2P_2$  are 4.690 and 5.060 Å, respectively. Although the metal–metal distances are different, the shorter P–P diagonal bond in the rhombus structures for the  $^1A_g$  states are almost invariant, leading to more acute P–M–P bond angles from Al to In. As seen from Table 5, the P–In–P apex angle of the  $^1A_g$  state for  $In_2P_2$  is 45.1°, which is the smallest, while the corresponding apex angles are 49.2° and 48.2° for  $Al_2P_2$  and  $Ga_2P_2$ , respectively. Evidently, the P–P

interaction does not seem to change as a function of the metal. The M–P rhombus sides increase uniformly from Al–P (2.521 Å) to 2.569 Å for Ga–P and 2.739 Å for In–P.

The trends in the geometries of the excited electronic states of these species are also similar to the ground states. That is, the P–P distance of a given state of  $Al_2P_2$  is akin to the corresponding distances for  $Ga_2P_2$  and  $In_2P_2$ . The M–P distances increase from Al to In, and likewise the M–M distances monotonically increase from Al to In.

There are many striking differences among the three clusters, particularly with respect to the ordering of the excited electronic states. In this aspect, although  $Al_2P_2$  is similar to  $Ga_2P_2$ , the heavier  $In_2P_2$  differs in many ways from the lighter analogues. For example, the  $^3A_u$  state is the first excited state for both  $Al_2P_2$  and  $Ga_2P_2$ , but  $^3B_{2g}$  is the first excited state for  $In_2P_2$ . The  $^3A_u$  excited state is formed by the promotion of an electron from the  $2b_{1u}$  orbital to the  $1b_{1g}$  LUMO, while the  $^3B_{2g}$  excited state is formed by the promotion of an electron from the  $1b_{3g}$  to the  $1b_{1g}$  LUMO relative to the ground state. This is a consequence of the fact that the  $2b_{1u}$  orbital is the HOMO orbital for  $Al_2P_2$  and  $Ga_2P_2$ , while in the case of  $In_2P_2$ , the  $1b_{3g}$  orbital is the HOMO.

Whereas the ground states of  $Al_2P_2^+$  and  $Ga_2P_2^+$  positive ions are the same ( $^2B_{1u}$ ), the ground state of  $In_2P_2^+$  is the  $^2B_{3g}$  state. This variation is consistent with the difference in the HOMO of the heavier cluster from the lighter analogues. As seen from Table 5, some excited electronic states are farther apart from the ground state as one goes down the group. For example, the energy separations of the  $^3A_u$  state relative to the ground states of the three species are 0.86, 1.18, and 1.58 eV, respectively. A similar trend is noted for the  $^1A_u$  excited states. However, the  $^3B_{2g}$  and  $^1B_{2g}$  pairs exhibit a different trend in that the energy separations increase while going from Al to Ga but decrease while going from Ga to In. This anomaly is a consequence of relativistic effects<sup>28,29</sup> on In as explained on the basis of the Mulliken population analysis outlined below.

Table 6 compares the Mulliken populations for the electronic states of  $M_2P_2$ . Evidently, all the electronic states exhibit charge transfer from M to P leading to  $M^+P^-$  ionic bonds in  $M_2P_2$ . As seen from Table 6, the trend is interesting in that the charge transfers from the metal to P decrease from Al to Ga, but In differs by extending greater charge transfer to P.

The differences in the relative ordering of the electronic states may be explained through the Mulliken populations. As seen from Table 6, the formation of the  $^3A_u$  state requires promotion of electronic density from metal(s) to metal (p) as evidenced from substantially reduced metal (s) populations and enhanced

**TABLE 6: Comparison of Mulliken Populations for the Electronic States of  $M_2P_2$  in Rhombus Structure ( $M = Al, Ga, In$ )**

system	state ( $D_{2h}$ )	total		gross population						overlap M–P
		M	P	M(s)	M(p)	M(d)	P(s)	P(p)	P(d)	
$Al_2P_2$	$^1A_g$	2.676	5.324	1.829	0.754	0.093	1.820	3.336	0.169	0.274
	$^3A_u$	2.634	5.366	1.595	0.923	0.117	1.810	3.413	0.143	0.710
	$^1A_u$	2.643	5.357	1.570	0.955	0.118	1.808	3.405	0.144	0.733
	$^3B_{3u}$	2.680	5.320	1.389	1.162	0.129	1.795	3.415	0.111	1.687
	$^3B_{2g}$	2.590	5.410	1.834	0.672	0.084	1.836	3.409	0.166	0.242
$Ga_2P_2$	$^1A_g$	2.725	5.275	1.842	0.787	0.097	1.813	3.299	0.164	0.443
	$^3A_u$	2.746	5.254	1.672	0.956	0.117	1.802	3.313	0.139	0.765
	$^1A_u$	2.750	5.250	1.651	0.981	0.118	1.808	3.309	0.133	0.778
	$^3B_{2g}$	2.646	5.354	1.851	0.701	0.094	1.826	3.366	0.162	0.407
	$^1B_{2g}$	2.656	5.344	1.854	0.709	0.094	1.829	3.354	0.160	0.403
$In_2P_2$	$^1A_g$	2.605	5.395	1.841	0.714	0.050	1.842	3.395	0.158	0.334
	$^3B_{2g}$	2.538	5.462	1.847	0.637	0.054	1.854	3.452	0.156	0.314
	$^3A_u$	2.571	5.429	1.660	0.851	0.060	1.856	3.446	0.127	0.614
	$^1A_u$	2.574	5.426	1.635	0.878	0.061	1.854	3.444	0.128	0.638
	$^1B_{2g}$	2.552	5.448	1.854	0.643	0.054	1.855	3.438	0.156	0.313

M(p) populations in these states. This process is unfavorable for In due to the relativistic mass–velocity contraction<sup>28,29</sup> for In which stabilizes the 5s orbital of the In atom in comparison to the 4s and 3s orbitals of Ga and Al. Consequently, the 5s–5p promotion energy is larger for In compared to that of the lighter analogues (Al, Ga). On the other hand, the <sup>3</sup>B<sub>2g</sub> state has similar M(s) and M(p) populations compared to the ground state, and thus this state is relatively more favored for In<sub>2</sub>P<sub>2</sub> due to the relativistic mass–velocity stabilization of the 5s orbital of In.

The metal–phosphorus overlap populations increase from Al to Ga but decrease from Ga to In uniformly. As noted above, this feature seems to arise from the relativistic mass–velocity stabilization of the 5s orbital of In, resulting in generally weaker In–P bonds and overlaps. The P populations are quite similar, suggesting that the differences in the properties arise primarily due to the relativistic effects for the heavier in atoms. The M(d) populations are smaller for In compared to the lighter species.

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