Spectroscopic Properties of Al\(_2\)P\(_2\), Al\(_2\)P\(_2\)\(^+\), and Al\(_2\)P\(_2\)\(^-\) and Comparison with Their Ga and In Analogues

Ping Yi Feng\(^{1,2}\) and K. Balasubramanian*\(^{3,4}\)

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: May 10, 1999; In Final Form: August 10, 1999

Sixteen electronic states of Al\(_2\)P\(_2\), three states of Al\(_2\)P\(_2\)\(^+\), and the ground state of Al\(_2\)P\(_2\)\(^-\) are studied using the complete active-space MCSCF (CASSCF) followed by multireference singles + doubles configuration interaction (MRSDCI). The \(^1\)A\(_g\), \(^2\)B\(_{1u}\), and \(^2\)B\(_{1g}\) electronic states with rhombus equilibrium structures were found to be the ground states of Al\(_2\)P\(_2\), Al\(_2\)P\(_2\)\(^+\), and Al\(_2\)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 photodetachment spectroscopic studies of Neumark and co-workers. Comparison of electronic states of M\(_2\)P\(_2\) (M = Al, Ga, and In) was made. It is shown that the electronic states of In\(_2\)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.\(^{1–20}\) 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.\(^{1–13}\) 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.\(^{1–14}\) 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\(^{14}\) 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 Ga\(_x\)As\(_y\) clusters was revealed by this work, which revealed that the reactivity of isomers contrasted dramatically in the reactive etching of Ga\(_x\)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\(^{1–5}\) have studied a number of III–V semiconductor clusters employing anion photodetachment spectroscopic and zero electron kinetic energy spectroscopic techniques. The anion photodetachment 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 Al\(_2\)P\(_2\) clusters are yet to be made using these techniques, Neumark and co-workers\(^4\) have studied the related indium phosphide clusters containing 2–8 atoms using anion photodetachment spectroscopy of In\(_x\)P\(_y\)\(^-\) (x, y = 1–4). In another study Arnold and Neumark\(^1\) have investigated the electronic states of trimeric clusters of the formulas In\(_2\)P and 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\(^{13}\) 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 Ga\(_x\)As\(_y\) and related III–V clusters,\(^{9,11,15–20}\) there are relatively fewer studies of the aluminum phosphate clusters. The geometries and energy separations of the low-lying electronic states of gallium arsenide clusters\(^{9,11,16–19}\) have been obtained for
several smaller clusters. More recently, the authors\textsuperscript{19,20} 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 Al\textsubscript{2}P\textsubscript{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 Al\textsubscript{2}P\textsubscript{2}, Al\textsubscript{2}P\textsubscript{2}\textsuperscript{+}, and Al\textsubscript{2}P\textsubscript{2}\textsuperscript{−}. 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 Al\textsubscript{2}P\textsubscript{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\textsuperscript{2}3p\textsuperscript{3} and 3s\textsuperscript{2}3p\textsuperscript{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 (\(\alpha_\text{Al} = 0.3084\)) for Al and two sets of d functions (\(\alpha_{\text{Al}} = 1.20\) and \(\alpha_{\text{Al}} = 0.3\)) for P. In one of the authors'\textsuperscript{22} previous studies on the neutral Ga\textsubscript{2}As\textsubscript{2}, it was discovered that rhombus is the most favorable structure among the linear, trapezoidal, and rhombus isomers of Ga\textsubscript{2}As\textsubscript{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 Al–P–P–Al linear structure, and a trapezoidal structure. Full geometry optimization of all of 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 Al\textsubscript{2}P\textsubscript{2} was restricted to the rhombus structures. All final CASSCF and MRSDCI calculations were made in the \(D_3h\) 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\textsuperscript{23} 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 spanned an active space comprising two \(a_2\), one \(b_2\), two \(b_1\), one \(b_3\), two \(b_3\), one \(b_1\), and one \(b_2\) orbital in the \(D_3h\) symmetry group.

The optimized geometries of all possible singlet and triplet electronic states for Al\textsubscript{2}P\textsubscript{2} in \(D_3h\) 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 Al\textsubscript{2}P\textsubscript{2}\textsuperscript{+} and Al\textsubscript{2}P\textsubscript{2}\textsuperscript{−} 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 Al\textsubscript{2}P\textsubscript{2}\textsuperscript{+} and the ground state of Al\textsubscript{2}P\textsubscript{2}\textsuperscript{−} were computed. To gain insight into the properties of the molecules, the atomization energies were computed. This was accomplished sequentially first by dissociating the Al\textsubscript{2}P\textsubscript{2} cluster into two aluminum atoms (\(2\)P) and the P\textsubscript{2} molecule (\(\Sigma^+_g\)) in their ground states. Subsequently, the Al\textsubscript{2}P\textsubscript{2} cluster was atomized into two aluminum atoms (\(2\)P) and two phosphorus atoms (\(2\)S). All of these dissociations were made as supermolecular computations.

The MCSCF/MRSDCI calculations were made using one of the authors'\textsuperscript{24} modified version of ALCHEMY II codes\textsuperscript{25} to include relativistic ECPs (RECPs).

3. Results and Discussions

### Electronic States of Al\textsubscript{2}P\textsubscript{2}

The equilibrium geometries and energy separations for all singlet and triplet electronic states of Al\textsubscript{2}P\textsubscript{2} in rhombus structures (\(D_3h\) 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 Al\textsubscript{2}P\textsubscript{2} since the first excited \(^3\text{A}_g\) 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>
<thead>
<tr>
<th>System State</th>
<th>Al–Al</th>
<th>P–P</th>
<th>Al–P–P</th>
<th>E (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al\textsubscript{2}P\textsubscript{2}</td>
<td>(^1\text{A}_g)</td>
<td>4.600</td>
<td>2.123</td>
<td>2.533</td>
</tr>
<tr>
<td>Al\textsubscript{2}P\textsubscript{2}</td>
<td>(^1\text{B}_1)</td>
<td>4.086</td>
<td>2.379</td>
<td>61.6</td>
</tr>
<tr>
<td>Al\textsubscript{2}P\textsubscript{2}</td>
<td>(^1\text{B}_3)</td>
<td>4.084</td>
<td>2.372</td>
<td>61.5</td>
</tr>
<tr>
<td>\textsubscript{2}B\textsubscript{3u}</td>
<td>3.188</td>
<td>3.036</td>
<td>88.3</td>
<td>2.15</td>
</tr>
<tr>
<td>\textsubscript{2}B\textsubscript{3g}</td>
<td>4.729</td>
<td>2.161</td>
<td>55.3</td>
<td>1.76</td>
</tr>
<tr>
<td>\textsubscript{2}B\textsubscript{3u}</td>
<td>4.734</td>
<td>2.170</td>
<td>49.3</td>
<td>2.02</td>
</tr>
<tr>
<td>\textsubscript{2}B\textsubscript{3g}</td>
<td>3.793</td>
<td>3.032</td>
<td>77.3</td>
<td>2.35</td>
</tr>
<tr>
<td>\textsubscript{1}B\textsubscript{3g}</td>
<td>3.786</td>
<td>3.062</td>
<td>77.9</td>
<td>3.02</td>
</tr>
<tr>
<td>\textsubscript{1}B\textsubscript{1g}</td>
<td>4.107</td>
<td>2.481</td>
<td>58.3</td>
<td>3.15</td>
</tr>
<tr>
<td>\textsubscript{1}B\textsubscript{1u}</td>
<td>4.116</td>
<td>2.496</td>
<td>62.5</td>
<td>3.24</td>
</tr>
<tr>
<td>\textsubscript{1}B\textsubscript{3u}</td>
<td>3.731</td>
<td>3.331</td>
<td>85.5</td>
<td>3.48</td>
</tr>
<tr>
<td>\textsubscript{1}B\textsubscript{3g}</td>
<td>3.747</td>
<td>3.466</td>
<td>55.5</td>
<td>4.10</td>
</tr>
<tr>
<td>\textsubscript{1}B\textsubscript{1u}</td>
<td>4.039</td>
<td>2.543</td>
<td>64.4</td>
<td>4.29</td>
</tr>
<tr>
<td>\textsubscript{1}B\textsubscript{2g}</td>
<td>4.612</td>
<td>2.188</td>
<td>50.8</td>
<td>4.48</td>
</tr>
</tbody>
</table>

Table 1: Geometries (Distances in Å and Angles in deg) and Energy Separations (E, in eV) for the Electronic States of Al\textsubscript{2}P\textsubscript{2}, Al\textsubscript{2}P\textsubscript{2}\textsuperscript{+}, and Al\textsubscript{2}P\textsubscript{2}\textsuperscript{−} with Rhombus Geometries at the CASSCF Level.
TABLE 2: Geometries (Distances in Å and Angles in deg) and Energy Separations (E, in eV) for the Electronic States of Al₂P₂, Al₂P⁺, and Al₂P⁻ in Rhombus Structures at the MRSDCI Level

<table>
<thead>
<tr>
<th>system</th>
<th>state</th>
<th>Al−Al</th>
<th>P−P</th>
<th>Al−P</th>
<th>P−Al−P</th>
<th>E⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂P₂</td>
<td>¹A₁g</td>
<td>4.584</td>
<td>2.100</td>
<td>2.521</td>
<td>49.2</td>
<td>0.00 (0.00)</td>
</tr>
<tr>
<td></td>
<td>¹A₂g</td>
<td>4.105</td>
<td>2.356</td>
<td>2.367</td>
<td>59.7</td>
<td>1.12 (0.86)</td>
</tr>
<tr>
<td></td>
<td>¹A₄g</td>
<td>4.089</td>
<td>2.370</td>
<td>2.362</td>
<td>60.1</td>
<td>1.22 (1.00)</td>
</tr>
<tr>
<td></td>
<td>²B₁₂g</td>
<td>3.173</td>
<td>3.333</td>
<td>2.303</td>
<td>92.7</td>
<td>1.41 (1.12)</td>
</tr>
<tr>
<td></td>
<td>²B₂₂g</td>
<td>4.695</td>
<td>2.130</td>
<td>2.578</td>
<td>48.8</td>
<td>1.50 (1.40)</td>
</tr>
<tr>
<td></td>
<td>²B₃₂g</td>
<td>3.168</td>
<td>3.350</td>
<td>2.305</td>
<td>93.2</td>
<td>1.92 (1.64)</td>
</tr>
<tr>
<td></td>
<td>²B₄₂g</td>
<td>4.706</td>
<td>2.125</td>
<td>2.582</td>
<td>48.6</td>
<td>2.08 (2.02)</td>
</tr>
<tr>
<td></td>
<td>²B₅₂g</td>
<td>4.588</td>
<td>2.367</td>
<td>2.581</td>
<td>54.6</td>
<td>2.24 (2.27)</td>
</tr>
<tr>
<td></td>
<td>²B₆₂g</td>
<td>3.804</td>
<td>2.934</td>
<td>2.402</td>
<td>75.3</td>
<td>2.65 (2.27)</td>
</tr>
<tr>
<td></td>
<td>²B₇₂g</td>
<td>3.804</td>
<td>2.892</td>
<td>2.389</td>
<td>74.5</td>
<td>2.81 (2.41)</td>
</tr>
<tr>
<td></td>
<td>²B₈₂g</td>
<td>4.083</td>
<td>2.388</td>
<td>2.365</td>
<td>60.6</td>
<td>3.03 (2.79)</td>
</tr>
<tr>
<td></td>
<td>²B₉₂g</td>
<td>4.069</td>
<td>2.371</td>
<td>2.355</td>
<td>60.5</td>
<td>3.09 (2.84)</td>
</tr>
<tr>
<td></td>
<td>²B₁₀₂g</td>
<td>3.746</td>
<td>3.200</td>
<td>2.463</td>
<td>81.0</td>
<td>3.30 (3.07)</td>
</tr>
<tr>
<td></td>
<td>²B₁₁₂g</td>
<td>3.755</td>
<td>3.222</td>
<td>2.474</td>
<td>81.3</td>
<td>3.59 (3.30)</td>
</tr>
<tr>
<td></td>
<td>²B₁₂₂g</td>
<td>4.078</td>
<td>2.444</td>
<td>2.377</td>
<td>61.9</td>
<td>4.18 (3.75)</td>
</tr>
<tr>
<td></td>
<td>³A₁g</td>
<td>4.593</td>
<td>2.131</td>
<td>2.532</td>
<td>49.8</td>
<td>4.76 (4.55)</td>
</tr>
</tbody>
</table>

2Al(²P) + 2P(²S)  

9.80 (8.92)  

The values in the parentheses are the Davidson corrected energies.

The P−P bond length in the ¹A₁g state of Al₂P₂ at the CASSCF level is longer than the corresponding bond length of the ²Σg⁻+ ground state of P₂, which is 1.8934 Å.²⁶ This suggests that the P−P diagonal interaction in Al₂P₂ is weaker than a triple bond in P₂ 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 ¹A₁g state of Al₂P₂ is 4.600 Å. Since the Al−Al bond length in the ²Σg⁻+ ground state of P₂ is 2.521 Å at the CASSCF level,²⁷ the Al−Al bonding in Al₂P₂ 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 Al₂P₂.

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 closest 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 Al₂P₂ 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 ¹A₂g, ¹A₄g, and ¹A₄u 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 ¹A₁g and ¹A₂g states are 1.29 and 1.34 eV higher than the ¹A₂g 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 Al₂P₂, 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 D₂h symmetry. In particular, a T structure may be feasible for some higher-lying excited states of Al₂P₂. 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 ¹A₁g ground state are to the ¹B₁₁g, ¹B₂₁g, and ¹B₃₁g excited states. As seen from Table 2, these states lie at 1.93 (¹B₁₁g), 3.99 (¹B₂₁g), and 4.18 eV (¹B₃₁g) 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 ¹B₃₁g 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 Al₂P⁻ and compare them with the corresponding spectra reported by Neumark and co-workers for In₂P⁻.

The atomization energy for Al₂P₂ was computed sequentially as a supermolecular computation. As seen from Table 2, the energy required to break the Al−P bonds in the Al₂P₂ cluster resulting in two Al atoms (²P) and the P₂ (²Σ⁺) 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 Al₂P₂ into two Al(²P) and two phosphorus atoms (²S) 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 Al₂P₂ and plays a more important role in the properties for the electronic states of Al₂P₂.

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 Al₂P₂ exhibit charge transfers from Al to P resulting in Al¹⁺P⁻ 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 Al₂P₂ 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 4 shows the leading electronic configurations for the electronic states of Al$_2$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 $1a_g$ orbital is [P$_1$(p$_x$), P$_2$(p$_x$)] and it is a bonding orbital in which two phosphorus atoms furnishes lobes on the phosphorus diagonal, resulting in a bonding interaction between two phosphorus atoms. The 1b$_{1g}$ orbital is [P$_1$(p$_x$) - P$_2$(p$_x$)], which is an antibonding 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 orbitals composed of [P$_1$(p$_x$) + P$_2$(p$_x$)], and [Al$_1$(p$_x$) + Al$_2$(p$_x$)], respectively. The 1b$_{1g}$ antibonding orbital is made of [P$_1$(p$_x$) - P$_2$(p$_x$)], while the 1b$_{2g}$ orbital is [Al$_1$(p$_x$) + Al$_2$(p$_x$)], and it is a bonding orbital between two aluminum atoms.

In the $1^A_g$ ground state, the 3a$_{1g}$, 2b$_{2u}$, 1b$_{1g}$, 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 $1^A_g$ ground state of Al$_2$P$_2$. For example, the differences in the properties of the $1^A_g$ ground state and the $2^A_g$ 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 $1^A_g$ but half-filled in $2^A_g$, while...
the 1b1g antibonding π orbital between the P atoms is singly occupied in 3A_u.

The nature of the orbitals facilitates rationalization of the Mulliken populations. As seen from the Table 3, the gross Al(s) population of the 1A_g state is 1.829, which is larger than the relevant value of 1.595 for 1A_u. On the contrary, the gross P(p) population for the 1A_g (3.363) is smaller than the corresponding value for 1A_u (3.413). This is a consequence of the fact that the Al(s) is the main part of the 2b1u orbital, while the 1b1g orbital is composed mainly of P(p).

The Electronic States of Al2P2+ and Al2P2+ and Predictions of Photoionization Spectra of Al2P2+.

An important property of a cluster is the first ionization energy of the cluster. The vertical ionization energies of Al2P2+ to three possible low-lying states of Al2P2+ 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 2B1u, 2B3g, and 2B3u states for the positive ion. Removal of an electron from the 2b1u HOMO of the 1A_g state leads to the 1B3u state, which is the ground state of Al2P2+. Thus, the vertical ionization energy of Al2P2+ to yield the 2B1u state is computed as 7.04 and 7.38 eV at the CASSCF and MRSDCI levels, respectively. The first excited state of the Al2P2+ ion is 2B3g, which is formed from the neutral 1A_g state by the removal of an electron from the 1b1g orbital, and the vertical ionization energy needed is 7.19 eV at the MRSDCI level. Consequently, the 2B3g 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 1b1u orbital in 1A_g is 9.35 eV (at the MRSDCI level), which is considerably higher resulting in the 2B3u state of Al2P2+. From the Mulliken population comparison between the 1A_g and 2B1u states, it is seen that in the 2B1u state of Al2P2+ there is a clear depletion of the 3p population on Al atoms after the ionization process. This is fully consistent with the nature of the 2b1u orbital, since the orbital is primarily composed of Al(3s). In the 1A_g state, the 2b1u orbital is fully occupied. Since an electron is removed from 2b1u after ionization, the Al(3s) population is decreased analogous to the 2B1u state of Al2P2+. Since the 1b1g orbital is mainly made of P(3p) and the 1A_g state has full occupancy for the 1b1g orbital, removal of an electron from 1b1g results in a decrease of the P(3p) population in the 2B1g state of Al2P2+.

Next consider the Al2P2− anion and predictions of the anion photodetachment spectra of Al2P2−. The ground electronic state of the anion was computed to be a 2B1g state. The equilibrium geometry and the adiabatic electron affinity (EA) of the 2B1g 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 2B1g 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 1A_g ground state of the neutral Al2P2 at the same levels. The Al−P bond lengths of the 2B1g state also shrink a bit, while the P−P bond length is a bit elongated in comparison to the corresponding bond lengths of the 1A_g state of Al2P2. 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 Al2P2− anion is formed by adding an electron to the 1b1g LUMO of the 1A_g state of the neutral Al2P2, resulting in the 2B1g state of Al2P2−. As shown before, the 1b1g orbital is composed of P(p)−P(3p), which is an antibonding π 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 Al2P2− anion. The Mulliken population analysis reveals that the s populations on Al and P atoms in the 2B1g state of Al2P2− are smaller, while the p populations on these two atoms are larger compared to the corresponding populations of the 1A_g state of neutral Al2P2, consistent with the composition of the LUMO which is primarily composed of the 3p orbitals of Al and P atoms. The adiabatic electron affinity (EA of Al2P2−) 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-workers1−5 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 Al2P2 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.4 have obtained the anion photoelectron spectra of In2P2− for x, y = 1−4. It is therefore of interest to compare our computational results with the analogous In2P2− observed by Xu et al. The PES spectra of In2P2− exhibit three distinct peaks labeled X, A, and B, where X corresponds to the ground state of In2P2 and the A and B states are excited states of the neutral In2P2. 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 In2P2 are 1.2 and 2.0 eV above the X ground state, respectively. Our previous study on In2P230 revealed that the 3B2g excited state of In2P2 lies 1.26 eV above the 1A_g ground state. There are three electronic states near the 1.6 eV region, namely, 3A_u, 1A_u, and 1B2g states. The current authors thus assigned the A peak of the photoelectron spectrum of In2P2− of Xu et al. to the 3B2g excited state of In2P2. However, unambiguous assignment of the observed B state could not be made due to the existence of the 3B2u and 3B1u 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 Al2P2−. The lowest energy peak for the neutral Al2P2, 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 Al2P2 are likely to be more accurate than the electron affinity of Al2P2. As seen from Table 2, the excited electronic states of Al2P2 are considerably more clustered and complex compared to those of In2P2. This would result in several overlapping bands in the anion photoelectron spectra. The lowest excited 3A_u 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 1A_u and 3B1u states are 1.00 and 1.12 eV higher than the 1A_g 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 3B2g and 3B1u excited states are 1.40 and 1.64 eV higher than the 1A_g 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 In2P2. Overall, we expect the anion spectra of
the Al bond length in the 1A_g state of Al₂P₂ is 4.584 Å, which is
a consequence of the fact that the 2b₁₁ orbital is the HOMO orbital for Al₂P₂
and Ga₂P₂, but 3B₂g is the first excited state for In₂P₂. The 1A_u excited state is formed
by the promotion of an electron from the 2b₁₁ orbital to the 1b₁₉ LUMO, while the 3B₂g excited
state is formed by the promotion of an electron from the 1b₁₉ to the 1b₃₁ LUMO relative
to the ground state. This is a consequence of the fact that the 2b₁₁ orbital is the HOMO orbital
for Al₂P₂ and Ga₂P₂, while in the case of In₂P₂, the 1b₃₁ orbital is the HOMO.

Whereas the ground states of Al₂P₂⁺ and Ga₂P₂⁺ positive ions are the same (2B₁₁), the ground state of In₂P₂⁺ is the 3B₂g 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 1A_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 3B₂g and 1B₂g 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 effects²⁸,²⁹ 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 Al₂P₂. Evidently, all the electronic states exhibit charge transfer from M to P leading to M⁺P⁻ ionic bonds in M₂P₂. 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 1A_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 M₂P₂ in Rhombus Structure (M = Al, Ga, In)

<table>
<thead>
<tr>
<th>system</th>
<th>state (D₃h)</th>
<th>M⁻P</th>
<th>M⁻P</th>
<th>M⁻P</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂P₂</td>
<td>1A_g</td>
<td>2.676</td>
<td>5.324</td>
<td>1.829</td>
<td>0.754</td>
</tr>
<tr>
<td></td>
<td>1A_u</td>
<td>2.634</td>
<td>5.366</td>
<td>1.595</td>
<td>0.923</td>
</tr>
<tr>
<td></td>
<td>3B₁ₙ</td>
<td>2.643</td>
<td>5.357</td>
<td>1.570</td>
<td>0.955</td>
</tr>
<tr>
<td></td>
<td>3B₂g</td>
<td>2.680</td>
<td>5.320</td>
<td>1.389</td>
<td>1.162</td>
</tr>
<tr>
<td>Ga₂P₂</td>
<td>1A_g</td>
<td>2.725</td>
<td>5.275</td>
<td>1.842</td>
<td>0.787</td>
</tr>
<tr>
<td></td>
<td>1A_u</td>
<td>2.672</td>
<td>5.254</td>
<td>1.672</td>
<td>0.956</td>
</tr>
<tr>
<td></td>
<td>3B₁ₙ</td>
<td>2.646</td>
<td>5.354</td>
<td>1.851</td>
<td>0.701</td>
</tr>
<tr>
<td></td>
<td>3B₂g</td>
<td>2.656</td>
<td>5.344</td>
<td>1.854</td>
<td>0.709</td>
</tr>
<tr>
<td>In₂P₂</td>
<td>1A_g</td>
<td>2.605</td>
<td>5.395</td>
<td>1.841</td>
<td>0.714</td>
</tr>
<tr>
<td></td>
<td>1A_u</td>
<td>2.538</td>
<td>5.462</td>
<td>1.847</td>
<td>0.637</td>
</tr>
<tr>
<td></td>
<td>3B₁ₙ</td>
<td>2.571</td>
<td>5.429</td>
<td>1.660</td>
<td>0.851</td>
</tr>
<tr>
<td></td>
<td>3B₂g</td>
<td>2.574</td>
<td>5.426</td>
<td>1.635</td>
<td>0.878</td>
</tr>
<tr>
<td></td>
<td>1B₂g</td>
<td>2.552</td>
<td>5.448</td>
<td>1.854</td>
<td>0.643</td>
</tr>
</tbody>
</table>
M(p) populations in these states. This process is unfavorable for In due to the relativistic mass—velocity contraction$^{28,29}$ 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 $^3\text{B}_2$ state has similar M(s) and M(p) populations compared to the ground state, and thus this state is relatively more favored for In 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.

Acknowledgment. This research was supported by National Science Foundation under grant no. CHE9814056.

References and Notes

(25) The major authors of ALHEMY II are B. Liu, B. Lengsfield, and M. Yoshimine.