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Spectroscopic Properties of Al_2P_2, $Al_2P_2^+$, and $Al_2P_2^-$ and Comparison with Their Ga and In Analogues

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Sixteen electronic states of Al_2P_2, three states of $Al_2P_2^+$, and the ground state of $Al_2P_2^-$ are studied using the complete active-space MCSCF (CASSCF) followed by multireference singles + doubles configuration interaction (MRSDCI). The ^1A_g, $^2B_{1u}$, and $^2B_{1g}$ electronic states with rhombus equilibrium structures were found to be the ground states of Al_2P_2, $Al_2P_2^+$, and $Al_2P_2^-$, 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 M_2P_2 (M = Al, Ga, and In) was made. It is shown that the electronic states of In_2P_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_xAs_y clusters was revealed by this work, which revealed that the reactivity of isomers contrasted dramatically in the reactive etching of $Ga_xAs_y^-$ 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 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 Al_xP_y 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 photoelectron spectroscopy of $In_xP_y^-$ (x, y = 1−4). In another study Arnold and Neumark[3] have investigated the electronic states of trimeric clusters of the formulas In_2P 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_xAs_y and related III−V clusters,[9,11,15−20] 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[9,11,16−19] have been obtained for

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several smaller clusters. More recently, the authors[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_2P_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_2P_2, $Al_2P_2^+$, and $Al_2P_2^-$. 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 Al_2P_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'[22] previous studies on the neutral Ga_2As_2, it was discovered that rhombus is the most favorable structure among the linear, trapezoidal, and rhombus isomers of Ga_2As_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 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_2P_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[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_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.

TABLE 1: Geometries (Distances in Å and Angles in deg) and Energy Separations (*E*, in eV) for the Electronic States of Al_2P_2, $Al_2P_2^+$, and $Al_2P_2^-$ with Rhombus Geometries at the CASSCF Level

system	state	Al−Al	P−P	Al−P	P−Al−P	*E*
Al_2P_2	^1A_g	4.600	2.123	2.533	49.5	0.00
	^3A_u	4.086	2.436	2.379	61.6	1.29
	^1A_u	4.084	2.432	2.377	61.5	1.34
	$^3B_{3u}$	3.188	3.366	2.318	93.1	1.45
	$^3B_{2g}$	4.729	2.161	2.600	49.1	1.55
	$^3B_{2u}$	4.577	2.439	2.593	56.1	1.96
	$^1B_{2g}$	4.734	2.170	2.604	49.3	2.02
	$^1B_{3u}$	3.194	3.387	2.328	93.4	2.02
	$^3B_{3g}$	3.793	3.032	2.428	77.3	2.88
	$^1B_{3g}$	3.786	3.062	2.435	77.9	3.02
	$^1B_{1g}$	4.107	2.481	2.399	62.3	3.15
	$^3B_{1g}$	4.116	2.496	2.407	62.5	3.24
	$^3B_{1u}$	3.731	3.331	2.501	83.5	3.48
	$^1B_{1u}$	3.747	3.466	2.552	85.5	4.10
	$^1B_{2u}$	4.039	2.543	2.386	64.4	4.29
	^3A_g	4.612	2.188	2.552	50.8	4.48
$Al_2P_2^+$	$^2B_{1u}$	4.584	2.100	2.521	49.2	7.04
	$^2B_{3g}$	4.584	2.100	2.521	49.2	7.19
	$^2B_{3u}$	4.584	2.100	2.521	49.2	9.01
$Al_2P_2^-$	$^2B_{1g}$	4.268	2.300	2.424	55.6	−0.57

The optimized geometries of all possible singlet and triplet electronic states for Al_2P_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 ≥ 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 $Al_2P_2^+$ positive and $Al_2P_2^-$ 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 $Al_2P_2^+$ and the ground state of $Al_2P_2^-$ were computed. To gain insight into the properties of the molecules, the atomization energies were computed. This was accomplished sequentially first by dissociating the Al_2P_2 cluster into two aluminum atoms (^2P) and the P_2 molecule ($^1\Sigma_g^+$) in their ground states. Subsequently, the Al_2P_2 cluster was atomized into two aluminum atoms (^2P) and two phosphorus atoms (^4S). All of these dissociations were made as supermolecular computations.

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

3. Results and Discussions

Electronic States of Al_2P_2. The equilibrium geometries and energy separations for all singlet and triplet electronic states of Al_2P_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 ^1A_g state is unambiguously the ground state of Al_2P_2 since the first excited ^3A_u state is considerably higher than the ground state (1.29 eV). At the CASSCF level, the P−P diagonal bond length of the ^1A_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_2P_2, $Al_2P_2^+$, and $Al_2P_2^-$ in Rhombus Structures at the MRSDCI Level

system	state	Al−Al	P−P	Al−P	P−Al−P	E^a
Al_2P_2	^1A_g	4.584	2.100	2.521	49.2	0.00 (0.00)
	^3A_u	4.105	2.356	2.367	59.7	1.12 (0.86)
	^1A_u	4.089	2.370	2.362	60.1	1.22 (1.00)
	$^3B_{3u}$	3.179	3.333	2.303	92.7	1.41 (1.12)
	$^3B_{2g}$	4.695	2.130	2.578	48.8	1.50 (1.40)
	$^1B_{3u}$	3.168	3.350	2.305	93.2	1.93 (1.64)
	$^1B_{2g}$	4.706	2.125	2.582	48.6	2.08 (2.02)
	$^3B_{2u}$	4.588	2.367	2.581	54.6	2.24 (2.27)
	$^3B_{3g}$	3.804	2.934	2.402	75.3	2.65 (2.27)
	$^1B_{3g}$	3.804	2.892	2.389	74.5	2.81 (2.41)
	$^1B_{1g}$	4.083	2.388	2.365	60.6	3.03 (2.79)
	$^3B_{1g}$	4.069	2.371	2.355	60.5	3.09 (2.84)
	$^3B_{1u}$	3.746	3.200	2.463	81.0	3.30 (2.93)
	$^1B_{1u}$	3.755	3.222	2.474	81.3	3.99 (3.60)
	$^1B_{2u}$	4.078	2.444	2.377	61.9	4.18 (3.75)
	^3A_g	4.593	2.131	2.532	49.8	4.76 (4.55)
$2Al(^2P) + P_2(^1\Sigma_g^+)$						3.87 (3.89)
$2Al(^2P) + 2P(^4S)$						8.90 (8.92)
$Al_2P_2^+$	$^2B_{1u}$	4.584	2.100	2.521	49.2	7.38 (7.20)
	$^2B_{3g}$	4.584	2.100	2.521	49.2	7.84 (7.76)
	$^2B_{3u}$	4.584	2.100	2.521	49.2	9.35 (9.04)
$Al_2P_2^-$	$^2B_{1g}$	4.282	2.242	2.417	55.3	−1.09 (−1.33)

[a] The values in the parentheses are the Davidson corrected energies.

The P−P bond length in the ^1A_g state of Al_2P_2 at the CASSCF level is longer than the corresponding bond length of the $^1\Sigma_g^+$ ground state of P_2, which is 1.8934 Å.[26] This suggests that the P−P diagonal interaction in Al_2P_2 is weaker than a triple bond in P_2 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 ^1A_g state of Al_2P_2 is 4.600 Å. Since the Al−Al bond length in the $^2A_1$ ground state of Al_3 is 2.521 Å at the CASSCF level,[27] the Al−Al bonding in Al_2P_2 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_2P_2.

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_2P_2 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 ^1A_g, ^3A_u, and ^1A_u 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 ^3A_u and ^1A_u states are 1.29 and 1.34 eV higher than the ^1A_g 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_2P_2, 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_{2h} symmetry. In particular, a T structure may be feasible for some higher-lying excited states of Al_2P_2. 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 ^1A_g ground state are to the $^1B_{1u}$, $^1B_{2u}$, and $^1B_{3u}$ excited states. As seen from Table 2, these states lie at 1.93 ($^1B_{3u}$), 3.99 ($^1B_{1u}$), and 4.18 eV ($^1B_{2u}$) 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 $^1B_{3u}$ 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 $Al_2P_2^-$ and compare them with the corresponding spectra reported by Neumark and co-workers[4] for $In_2P_2^-$.

The atomization energy for Al_2P_2 was computed sequentially as a supermolecular computation. As seen from Table 2, the energy required to break the Al−P bonds in the Al_2P_2 cluster resulting in two Al atoms (^2P) and the $P_2(^1\Sigma_g^+)$ 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_2P_2 into two $Al(^2P)$ and two phosphorus atoms (^4S) 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_2P_2 and plays a more important role in the properties for the electronic states of Al_2P_2.

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_2P_2 exhibit charge transfers from Al to P resulting in Al^+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 Al_2P_2 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 Al_2P_2, $Al_2P_2^+$, and $Al_2P_2^-$

		total		gross population						overlap
system	state (D_{2h})	Al	P	Al (s)	Al (p)	Al (d)	P (s)	P (p)	P (d)	Al−P
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
	$^1B_{3u}$	2.663	5.337	1.392	1.141	0.131	1.799	3.428	0.111	1.184
	$^1B_{2g}$	2.598	5.402	1.842	0.673	0.084	1.835	3.402	0.166	0.243
	$^3B_{2u}$	2.633	5.367	1.825	0.722	0.087	1.868	3.367	0.132	0.207
	$^3B_{3g}$	2.674	5.326	1.621	0.941	0.113	1.841	3.373	0.113	0.555
	$^1B_{3g}$	2.679	5.321	1.591	0.974	0.114	1.835	3.371	0.116	0.599
	$^1B_{1g}$	2.647	5.353	1.377	1.151	0.120	1.812	3.405	0.136	0.760
	$^3B_{1g}$	2.639	5.361	1.376	1.140	0.124	1.804	3.419	0.139	0.790
	$^3B_{1u}$	2.604	5.396	1.628	0.873	0.104	1.863	3.432	0.102	0.463
	$^1B_{1u}$	2.602	5.398	1.662	0.838	0.103	1.866	3.431	0.102	0.404
	$^1B_{2u}$	2.607	5.393	1.466	1.023	0.119	1.791	3.441	0.162	0.657
	^3A_g	2.634	5.366	1.477	1.066	0.092	1.820	3.379	0.167	0.255
$Al_2P_2^+$	$^2B_{1u}$	2.309	5.191	1.619	0.606	0.084	1.835	3.188	0.169	
	$^2B_{3g}$	2.464	5.036	1.884	0.493	0.087	1.838	3.022	0.176	
	$^2B_{3u}$	2.258	5.242	1.631	0.545	0.082	1.839	3.230	0.174	
$Al_2P_2^-$	$^2B_{1g}$	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 Al_2P_2, $Al_2P_2^+$, and $Al_2P_2^-$

			configurations												
system	state (D_{2h})	coeff	$1a_g$	$2a_g$	$3a_g$	$1b_{2u}$	$2b_{2u}$	$1b_{1u}$	$2b_{1u}$	$1b_{3g}$	$1b_{3u}$	$2b_{3u}$	$1b_{1g}$	$1b_{2g}$	$1a_u$
Al_2P_2	^1A_g	0.881	2	2	2	2	0	2	2	2	2	0	0	0	0
	^3A_u	0.885	2	2	2	2	0	2	1	2	2	0	1	0	0
	^1A_u	0.872	2	2	2	2	0	2	1	2	2	0	1	0	0
	$^3B_{3u}$	0.808	2	2	2	2	1	2	0	2	2	0	1	0	0
	$^3B_{2g}$	0.889	2	2	2	2	0	2	2	1	2	0	1	0	0
	$^1B_{3u}$	0.804	2	2	2	2	1	2	0	2	2	0	1	0	0
	$^1B_{2g}$	0.887	2	2	2	2	0	2	2	1	2	0	1	0	0
	$^3B_{2u}$	0.897	2	2	2	2	0	2	2	2	1	0	1	0	0
	$^3B_{3g}$	0.839	2	2	2	2	1	2	1	2	2	0	0	0	0
	$^1B_{3g}$	0.837	2	2	2	2	1	2	1	2	2	0	0	0	0
	$^1B_{1g}$	0.782	2	2	1	2	0	2	2	2	2	0	1	0	0
	$^3B_{1g}$	0.803	2	2	1	2	0	2	2	2	2	0	1	0	0
	$^3B_{1u}$	0.851	2	2	2	2	1	2	1	2	1	0	1	0	0
	$^1B_{1u}$	0.850	2	2	2	2	1	2	1	2	1	0	1	0	0
	$^1B_{2u}$	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
	^3A_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
$Al_2P_2^+$	$^2B_{1u}$	0.891	2	2	2	2	0	2	1	2	2	0	0	0	0
	$^2B_{3g}$	0.877	2	2	2	2	0	2	2	1	2	0	0	0	0
	$^2B_{3u}$	0.819	2	2	2	2	0	2	2	2	1	0	0	0	0
$Al_2P_2^-$	$^2B_{1g}$	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 Al_2P_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 Al_2P_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 $[Al_1(s) + Al_2(s)] - [P_1(s) + P_2(s)]$, and it is more localized orbital between the P atoms (and Al atoms). The $2b_{2u}$ orbital is made of $[P_1(p_y) + P_2(p_y)]$, and it is an antibonding σ 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 $[Al_1(s) - Al_2(s)]$ combined with $[Al_1(p_z) + Al_2(p_z)] - [P_1(p_z) + P_2(p_z)]$. Thus, the first part represents a repulsive interaction between two aluminum atoms, but the second part is a bonding π interaction between two phosphorus atoms. The $1b_{3g}$ orbital is $[P_1(p_z) - P_2(p_z)]$, which is an antibonding π 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 π 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 π 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 π orbital between two aluminum atoms.

In the ^1A_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 ^1A_g ground state of Al_2P_2. For example, the differences in the properties of the ^1A_g ground state and the ^3A_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 π bonding between two P atoms is fully occupied in ^1A_g but half-filled in ^3A_u, while the $1b_{1g}$ 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 ^3A_u. On the contrary, the gross P(p) population for the ^1A_g (3.336) is smaller than the corresponding value for ^3A_u (3.413). This is a consequence of the fact that the Al(s) is the main part of the $2b_{1u}$ orbital, while the $1b_{1g}$ orbital is composed mainly of P(p).

The Electronic States of $Al_2P_2^+$ and $Al_2P_2^-$ and Predictions of Photoionization Spectra of $Al_2P_2^-$. An important property of a cluster is the first ionization energy of the cluster. The vertical ionization energies of Al_2P_2 to three possible low-lying states of $Al_2P_2^+$ 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 $^2B_{1u}$, $^2B_{3g}$, and $^2B_{3u}$ states for the positive ion. Removal of an electron from the $2b_{1u}$ HOMO of the ^1A_g state leads to the $^2B_{1u}$ state, which is the ground state of $Al_2P_2^+$. Thus, the vertical ionization energy of Al_2P_2 to yield the $^2B_{1u}$ state is computed as 7.04 and 7.38 eV at the CASSCF and MRSDCI levels, respectively. The first excited state of the $Al_2P_2^+$ ion is $^2B_{3g}$, which is formed from the neutral ^1A_g state by the removal of an electron from the $1b_{3g}$ orbital, and the vertical ionization energy needed is 7.19 eV at the MRSDCI level. Consequently, the $^2B_{3g}$ 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 $1b_{3u}$ orbital in ^1A_g is 9.35 eV (at the MRSDCI level), which is considerably higher resulting in the $^2B_{3u}$ state of $Al_2P_2^+$. From the Mulliken population comparison between the ^1A_g and $^2B_{1u}$ states, it is seen that in the $^2B_{1u}$ state of $Al_2P_2^+$ 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 $2b_{1u}$ orbital, since the orbital is primarily composed of Al(3s). In the ^1A_g state, the $2b_{1u}$ orbital is fully occupied. Since an electron is removed from $2b_{1u}$ after ionization, the Al(3s) population is decreased analogous to the $^2B_{1u}$ state of $Al_2P_2^+$. Since the $1b_{3g}$ orbital is mainly made of P($3p_z$) and the ^1A_g state has full occupancy for the $1b_{3g}$ orbital, removal of an electron from $1b_{3g}$ results in a decrease of the P(3p) population in the $^2B_{3g}$ state of $Al_2P_2^+$.

Next we consider the $Al_2P_2^-$ anion and predictions of the anion photodetachment spectra of $Al_2P_2^-$. The ground electronic state of the anion was computed to be a $^2B_{1g}$ state. The equilibrium geometry and the adiabatic electron affinity (EA) of the $^2B_{1g}$ 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 $^2B_{1g}$ 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 Al_2P_2 at the same levels. The Al−P bond lengths of the $^2B_{1g}$ 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 Al_2P_2. 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 $Al_2P_2^-$ anion is formed by adding an electron to the $1b_{1g}$ LUMO of the ^1A_g state of the neutral Al_2P_2, resulting in the $^2B_{1g}$ state of $Al_2P_2^-$. As shown before, the $1b_{1g}$ orbital is composed of $P_1(p_x) - P_2(p_x)$, 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 $Al_2P_2^-$ anion. The Mulliken population analysis reveals that the s populations on Al and P atoms in the $^2B_{1g}$ state of $Al_2P_2^-$ are smaller, while the p populations on these two atoms are larger compared to the corresponding populations of the ^1A_g state of neutral Al_2P_2, 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_2P_2) 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[1−5] 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 can be determined. It appears that such spectroscopic studies on Al_2P_2 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 $In_xP_y^-$ for x, $y = 1-4$. It is therefore of interest to compare our computational results with the analogous In_2P_2 observed by Xu et al.[4] The PES spectra of $In_2P_2^-$ exhibit three distinct peaks labeled X, A, and B, where X corresponds to the ground state of In_2P_2 and the A and B states are excited states of the neutral In_2P_2. 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_2P_2 are 1.2 and 2.0 eV above the X ground state, respectively. Our previous study on In_2P_2[20] revealed that the $^3B_{2g}$ excited state of In_2P_2 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 $^1B_{2g}$ states. The current authors thus assigned the A peak of the photoelectron spectrum of $In_2P_2^-$ of Xu et al. to the $^3B_{2g}$ excited state of In_2P_2. However, unambiguous assignment of the observed B state could not be made due to the existence of the $^3B_{2u}$ and $^3B_{1u}$ 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 $Al_2P_2^-$. The lowest energy peak for the neutral Al_2P_2, 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_2P_2 are likely to be more accurate than the electron affinity of Al_2P_2. As seen from Table 2, the excited electronic states of Al_2P_2 are considerably more clustered and complex compared to those of In_2P_2. 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 $^3B_{3u}$ 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 $^3B_{2g}$ and $^1B_{3u}$ 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 In_2P_2. 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.[19,20] 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[28,29] 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 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)

		total		gross population						overlap
system	state (D_{2h})	M	P	M(s)	M(p)	M(d)	P(s)	P(p)	P(d)	M−P
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[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 $^3B_{2g}$ state has similar M(s) and M(p) populations compared to the ground state, and thus this state is relatively more favored for In_2P_2 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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