Electronic structure of the III–V tetramer clusters and their positive ions

D. W. Liao and K. Balasubramanian
Department of Chemistry, Arizona State University, Tempe, Arizona 85287-1604

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We study mixed group III–V tetramers and their positive ions, in particular, Al₂P₂, Ga₂As₂, In₂Sb₂, Tl₂Bi₂, and their positive ions. We employ ab initio complete active space multiconfiguration self-consistent field followed by multireference singles + doubles configuration interaction (MRSDCI) calculations. We also include the effects of spin–orbit coupling for Tl₂Bi₂ and In₂Sb₂ tetramers. The mixed III–V diatomics (AlP–TlBi) are also studied for comparison. Among the states and geometries considered here, we find that the lowest states of all four tetramers are A₁ with rhombus equilibrium geometries. We considered several excited states of the positive ions and found that the B₁u state with a rhombus geometry is the lowest for the positive ions. The binding energies and adiabatic ionization energies of all four tetramers are computed at the MRSDCI level and periodic trends are obtained. The Tl₂Bi₂ tetramer and TlBi dimer differ from their lighter analogs due to relativistic effects. We find that the binding energies per atom for the tetramers are larger than the trimers but comparable to the dimers.

I. INTRODUCTION

The electronic structure, spectroscopic properties, and the reactivities of mixed III–V clusters have been the topics of several experimental and theoretical studies in recent years. A possible motivation for a large number of these studies is that III–V materials are used in fast microelectronic devices since they are faster than conventional Si-type semiconductor materials. From a fundamental point, the nature of bonding and the observed ionization photofragmentation and reactivity patterns of the III–V clusters are quite intriguing. For example, O'Brien et al. have studied Ga₄As₅ clusters generated by laser vaporization of GaAs crystal. Mass analysis of the smaller clusters revealed substantial deviation from an expected binomial distribution. Likewise the photofragmentation of Ga₄As₅ cluster ions revealed differences in the fragmentation patterns of Si₄ and Ge₄ cluster ions. Several studies focused on the spectroscopic properties of III–V diatomics and their ions, such as GaAs, GaAs⁺, InSb, InSb⁺, AlP, etc. The recent works by Lemire et al. on the jet-cooled spectra of GaAs as well as the matrix-isolated electron-spin resonance (ESR) work of Knight and Petty are particularly interesting. A critical comparison of the experimentally derived spectroscopic constants with the theoretical values revealed that ab initio studies of these species could provide reliable spectroscopic data of these molecules. Theoretical studies of mixed III–V trimers have also been made.

While the properties of mixed dimers and trimers have been computed, this is not the case for the tetramers. At present, theoretical studies exist only on Ga₂As₂ and their ions. We note that the related Si₄ clusters have been studied intensely. The above survey reveals the need for theoretical studies which could provide data on structures and energetics. In addition, it would be important to gain insight into the nature of bonding, periodic trends, and the pattern of properties as a function of cluster size. In this study, we compute the geometries, binding energies, and ionization potentials (IPs) of the ground states of mixed III–V tetramers. In addition, we obtain the properties of several excited states of Al₂P₂⁺, Ga₂As₂⁺, In₂Sb₂⁺, and Tl₂Bi₂⁺. We also compute the properties of the corresponding dimers. At present, there are no spectroscopic data on TlBi. We use complete active space multiconfiguration self-consistent field/multireference singles + doubles configuration interaction/relativistic configuration-interaction calculational (CAS-MCSCF/MRSDCI/RCI) methods including spin–orbit coupling (especially for the heavier species).

II. METHOD OF CALCULATIONS

We start with a complete active space multiconfiguration self-consistent field (CAS-MCSCF) method. All four tetramers (Al₂P₂, Ga₂As₂, In₂Sb₂, Tl₂Bi₂) were oriented on the xz plane. We used uniformly relativistic effective core potentials (RECPs) for all four tetramers, although for Al₂P₂ relativistic effects may not be as important. The outermost ns²np² shells (n = principal quantum number) of the group III atom and the outermost ns²np³ shells of the group V atom were retained explicitly in the valence space in our calculations. The remaining core electrons were replaced by RECPs. The valence Gaussian basis sets and RECPs were taken from Refs. 37–39 for these elements. For Al and P, we contract the two large exponent s and p functions. All basis sets were augmented with one set of d polarization functions. The d⁴ Gaussian exponents for Al, P, Ga, As, In, Sb, TI, and Bi are 0.3084, 0.3909, 0.180, 0.220, 0.2129, 0.1305, 0.0789, 0.0804, 0.0809, 0.180, 0.220, 0.2129, 0.1305, 0.0789,
and 0.1463, respectively. The effective basis set is of (3s3p1d) quality and has been used before for GaAs (Ref. 24) and InSb (Ref. 16).

The CASSCF computation was made in the $D_{2h}$ symmetry. Since the group V ns$^2$ shells were much lower in energy excitations from these shells were not allowed in order to keep the CASSCF-configuration-interaction calculation (CI) dimension manageable. However, these orbitals were allowed to relax. The full active space of the ns and np orbitals of the group III atom and the np orbitals of the group V atom correlated into three $a_g$, three $b_{1u}$, two $b_{2u}$, two $b_{3g}$, one $b_{2g}$, and one $b_{1g}$ orbitals. Note that the two Group V ns orbitals which are not in the active space correlates into $a_g$ and $b_{2u}$. Full distribution of 12 active electrons (group V ns$^2$ inactive) in all possible ways among all these orbitals led to too big a CI space in the CASSCF. Consequently, the active space had to be restricted. We tried several possibilities and found that an active space which comprised two $a_g$, two $b_{1u}$, two $b_{2u}$, two $b_{3g}$, one $b_{2g}$, and one $b_{1g}$ was the optimal space of ten orbitals so that the number of configurations in the CASSCF was 3528 configuration spin functions (CSF).

The ground state of Ga$_3$As$_2$ is now well established to be a $^1A_g$ state. In the previous study on Ga$_3$As$_2$, the author considered other possible structures for Ga$_3$As$_2$, such as trapezium, linear, etc., and found the $^1A_g$ state with the rhombus structure to be the lowest. Furthermore, Meier et al. have considered other structures such as the T-shaped structure for Ga$_3$As$_2$ and found the rhombus structure to be the lowest. The rhombus structure is systematically favored for Al$_2$P$_2$-Tl$_2$Bi$_2$ since (i) the multiple bonding interaction between the group V atoms leads to a planar structure, (ii) rhombus structure leads to maximal interaction between III and V atoms (four such bonds), (iii) the shorter V-V bond length due to multiple bonding between these atoms leads to an acute rhombus structure than a square structure. Our previous study on all mixed III-V trimers has revealed the similarity of GaAs$_2$ and InSb$_2$. All these reasons support the rhombus structure as the ground state structure. We considered rhombus, T-shaped, and linear structures at single point geometries for Tl$_2$Bi$_2$ and find that the rhombus structure is favored. Both the III-V and V-V bond distances were optimized at the CASSCF.

For the positive ions of tetramers, we considered several electronic states based on the occupancies of natural orbitals of the ground states. An exhaustive study was made on Ga$_3$As$_2^+$. For this ion, we considered $^2B_{1u}$, $^2A_g$, $^2B_{2u}$, and $^2A_e$ electronic states. We found the $^2B_{1u}$ state as the lowest for Ga$_3$As$_2^+$. Hence calculations on other species included only $^2B_{1u}$ and $^2A_g$ states of the positive ions. The same active space was used for the positive ion as the neutral species. Separate CASSCF calculations were done for each state.

We carried out MRSDCI calculations beyond CASSCF. The MRSDCI method included excitations from all 16 electrons of the neutral tetramers. The MRSDCI included all configurations in the CASSCF with coefficients $>0.07$. We allowed single and double excitations from each of these reference configurations in the MRSDCI. Hence the MRSDCI method includes all important dynamic electron correlation effects. The MRSDCI of the positive ions included excitations of all 15 electrons with reference configurations chosen using the same criterion as the neutral molecule.

We computed the energy required to dissociate the tetramer into two dimers as a supermolecular calculation. The supermolecular calculation was done using a linear molecule with III-V-V-III geometry by setting III-V distances to the diatomic distance and V-V distances to 10 Å. The optimal active space for the linear orientation was found to be three $a_g$, three $b_{1u}$, one $b_{2u}$, one $b_{1g}$, one $b_{2g}$, and one $b_{1g}$. The computations of the dissociated species also retained the ns$^2$ shells of the group V atom in the inactive space so that the tetramer and dissociated species are treated alike.

The MRSDCI calculations of the dissociated species included single + double excitations from 16 electrons of these species from all reference configurations in the CASSCF with coefficients $>0.07$.

We also computed the spectroscopic constants of the mixed III-V diatomics with the objective of computing the atomization energies of the tetramers. Although GaAs and InSb have been studied before those computations were made at a higher second-order configuration interaction (SOCI) level of theory since they were focused on diatomics only. We use the CASSCF/MRSDCI method to compute the spectroscopic constants of the $^3\Sigma^-$ ground state of AlP, InSb, and TIBi. The CASSCF/MRSDCI calculations of the diatomics were made in the $C_{2v}$ group. All configurations in the CASSCF with coefficients $>0.07$ were included in the MRSDCI. The atomization energy (AE) of the tetramer is computed using the formula

$$AE(M,X_2) = D_e(M,X_2) + 2D_e(MM')$$

where $D_e(M,M')$ is the energy required to dissociate $M_2X_2$ into 2MX diatomics using the supermolecular calculation described above and $D_e$ is the dissociation energy of the III-V diatomic.

The spin–orbit effects could be important especially for TIBi, Tl$_2$Bi$_2$, In$_2$Sb$_2$, and InSb molecules. Consequently, we include the effect of spin–orbit coupling using the relativistic CI (RCI) method for these species. For TIBi, the $0^+$ state RCI calculations included reference configurations arising from $1\sigma^22\sigma^21\pi^2(\Sigma^-)$, $1\sigma^22\sigma^21\pi^2(\Sigma^+)$, $1\sigma^22\sigma1\pi^2(\Pi)$, $1\sigma^22\sigma2\pi1\sigma^2(\Pi)$, $1\sigma^21\pi^2(\Sigma^+)$. For Tl$_2$Bi$_2$, we find that the ground state is a close-shell $^1A_g$ state. Hence to first-order spin–orbit coupling is zero. We found only one triplet excited state of g symmetry which yields an $A_g$ state in the double group. We included 13 reference configurations in the RCI of Tl$_2$Bi$_2$ arising from these configurations. The spin–orbit effects were found to be rather small at the equilibrium geometry of the $^4A_g$ state since spin–orbit mixing from excited electronic states of Tl$_2$Bi$_2$ is rather small.

All CASSCF/MRSDCI calculations were made using one of the author's modified versions of ALCHEMII II codes to include relativistic effective core potentials (RECPs). The spin–orbit effects were included using the relativistic configuration interaction (RCI) method for polyatomics described in Ref. 43. We note that Pitzer and Win...
ter\textsuperscript{44} also outline procedures to include spin–orbit coupling using the double group CI.

III. RESULTS AND DISCUSSIONS

A. III–V dimers

Table I shows the computed CASSCF and MRSDCI spectroscopic constants of the III–V dimers. As seen from Table I, the $^{3}\Sigma^{-}$ ground state $r_s$ of AlP, GaAs, InSb, and TIBI are 2.38, 2.60, 3.00, and 3.50 Å, respectively. The results of GaAs are from a previous study.\textsuperscript{24} Our results on InSb and TIBI included spin–orbit effects.

We compute the $D_s$ of AlP, GaAs, InSb, and TIBI as 2.06, 1.6, 1.35, and 0.53 eV. The MRSDCI $D_s$ of TIBI includes the effect of spin–orbit coupling. The effects of $d$ correlations and further extension of the basis sets are known to increase the $D_s$ of GaAs. A value of 1.9 eV was predicted with this improvement.

An experimental value of 2.2 eV is predicted for the $D_s$ of AlP by DeMaria \textit{et al.}\textsuperscript{45} using the mass spectrometric method. Our computed $D_s$ value of AlP was also found to be in good agreement with the thermodynamic value of 1.4 eV corrected for the partition functions.

Grein and co-workers\textsuperscript{46,47} have studied several electronic states of both neutral AlP and Al$^{-}$ using the SCF/MRDCI method. For AlP they obtain a $X^{3}\Sigma^{-}$ ground state with $r_s = 4.64$ Å, and $\mu_s = 1.18$ D. Their best $D_s$ (basis set C)\textsuperscript{46} is 1.93 eV. These values compare very well with our $\mu_s = 1.19$ D and $D_s = 2.06$ eV. They use all-electron extended basis sets for AlP while we use ECPs. Hence the FCPs for Al and P give very comparable results to all-electron basis set results.

DeMaria \textit{et al.}\textsuperscript{48} have deduced a $D_s$ value of 1.2 eV for TIBI. This value is in disagreement with a rather low value of 0.53 eV obtained from our computations. Note that $D_0^s$(Sn$_2$) < $D_0^s$(InSb) and $D_0^s$(Si$_2$) < $D_0^s$(AlP).\textsuperscript{49} The $D_0^s$ values of Si$_2$, Ge$_2$, and Sn$_2$ and Pb$_2$ have been well established both experimentally and theoretically as 3.2, 2.8, 2.0, 0.82 eV, respectively.\textsuperscript{30} Evidently our computed and experimental $D_0^s$ of InSb near 1.4 eV are well below the $D_0^s$(Sn$_2$).\textsuperscript{49} Consequently, we expect the $D_s$(TIBI) < $D_s$(Pb$_2$). Since the $D_s$ of Pb$_2$ is established both experimentally\textsuperscript{49} and theoretically\textsuperscript{51} as 0.8 eV, we expect the $D_s$ of TIBI to be about 0.6 eV. Hence the $D_0^s$ of TIBI (1.2 eV) deduced by DeMaria \textit{et al.}\textsuperscript{48} is questioned.

DeMaria \textit{et al.}\textsuperscript{48} have used the Knudsen cell-mass spectrometric method to identify TIBI. From the thermodynamic data, they have deduced the $D_0^s$(TIBI) = 28 ± 3 kcal/mol or 1.2 eV which is too high compared to our computed value of 0.64 eV which reduces to 0.53 eV when corrected for spin–orbit coupling. They had assumed that the $r_s$ of TIBI = 2.73 Å which was based on the assumption that TIBI has a triple bond. Furthermore, they assume that the $\omega_s$ of the ground state is 118 cm$^{-1}$. As seen from Table I, the first assumption is grossly incorrect since the computed $r_s$ is 3.50 Å for TIBI. The vibrational frequency that we compute is also considerably lower.

The above $D_0^s$ value can be corrected using the formula

$$\delta D_0^s = RT \ln(q'/q^s),$$

where $q'$ and $q^s$ are the assumed and actual partition functions, respectively. We applied the above correction to both vibrational and rotational partition functions which yielded a $\delta D_0^s = -3$ kcal/mol at $T = 1500$ K. The corrected $D_0^s$ of 25 ± 3 kcal/mol is still too high since the $D_s$ of Pb$_2$ itself is only 0.8 eV or 18 kcal/mol.\textsuperscript{49} Consequently, revised thermodynamic data are warranted to estimate $D_0^s$(TIBI) more accurately since $D_0^s$(TIBI) must be less than $D_0^s$(Pb$_2$).

The spin–orbit coupling mixes the $^{3}\Sigma^{-}$ state of TIBI with the $^{1}\Sigma^+$ state strongly. Near its equilibrium geometry the $0^+$ state of TIBI is composed of 75% $^{3}\Sigma^{-}$ (1$\sigma^2$2$\sigma^2$3$\sigma^2$2$\pi^2$) and 16% $^{1}\Sigma^+$ (1$\sigma^2$2$\sigma^2$3$\sigma^2$2$\pi^2$). As distance increases different $\lambda$-states mix heavily leading to Ti + Bi dissociation. The spin–orbit coupling decreases the $\omega_s$ by 1 cm$^{-1}$ and decreases the bond distance by 0.01 Å.

All the vibrational frequencies in Table I were computed using a cubic polynomial fit and could thus have an uncertainty of up to 5%. However, we note that our computed $\omega_s$ of GaAs (215 cm$^{-1}$) is within 1 cm$^{-1}$ of the experimental value of 214 cm$^{-1}$ deduced by Lemire \textit{et al.}\textsuperscript{14}

B. Al$_3$P$_2$ and Al$_2$P$^+$

Table II shows the computed CASSCF and MRSDCI geometries of the ground state of Al$_3$P$_2$. As evidenced from that table the lowest state of Al$_3$P$_2$ is a $^1A_g$ state with an equilibrium structure of a rhombus. In a previous study on isoivalent Ga$_3$As$_2$ (Ref. 19), one of the authors considered other structures such as trapezium, four linear isomers, etc. Among these the rhombus structure was found to be the

\begin{table}[h]
\centering
\begin{tabular}{|l|c|c|c|c|c|c|}
\hline
Molecule & State & $R_s$ (Å) & $\omega_s$ (cm$^{-1}$) & $D_s$ (eV) & $R_s$ (Å) & $\omega_s$ (cm$^{-1}$) & $D_s$ (eV) \\
\hline
AlP & $^{3}\Sigma^{-}$ & 2.44 & 376 & 1.65 & 2.38 & 392 & 2.06 & 1.19 \\
GaAs* & $^{3}\Sigma^{-}$ & 2.92 & 134 & 1.11 & 3.00 & 136 & 1.35 & 2.27 \\
InSb & $^{3}\Sigma^{-}$ & 3.49 & 67 & 0.46 & 5.50 & 96 & 0.53 & 3.09 \\
TIBI\textsuperscript{b} & $^{3}\Sigma^{-}$ & 2.73 & 215 & 1.6 (1.9) & 1.34 & \\
\hline
\end{tabular}
\caption{Spectroscopic constants of the III–V diatomics.}
\end{table}

\textsuperscript{*}The data of GaAs are quoted from Ref. 24.

\textsuperscript{b}The MRSDCI results of TIBI include the effect of spin–orbit coupling.
higher in energy since the electron from a strongly bonding both P \((3p, \sigma)\) and Al from the highest occupied \(2b_{3u}\) orbital which is composed of the \(\pi-\) bonding type of the 

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Geometry</th>
<th>State</th>
<th>(r_{e1} (\text{Å})^a)</th>
<th>(r_{e2} (\text{Å})^b)</th>
<th>(\theta_{e} (^\circ)^c)</th>
<th>(E (\text{eV}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Al}_2\text{P}_2)</td>
<td>Rhombus</td>
<td>(^1A_g)</td>
<td>2.35</td>
<td>2.14</td>
<td>49.7</td>
<td>8.74</td>
</tr>
<tr>
<td>(\text{Al}_2\text{P}_2)</td>
<td>Rhombus</td>
<td>(^2B_{1u})</td>
<td>2.51</td>
<td>2.21</td>
<td>52.2</td>
<td>6.74</td>
</tr>
<tr>
<td>(\text{Al}_2\text{P}_2)</td>
<td>Rhombus</td>
<td>(^2A_g)</td>
<td>2.55</td>
<td>2.12</td>
<td>49.1</td>
<td>8.74</td>
</tr>
<tr>
<td>(2(\text{AlP}))</td>
<td>Linear</td>
<td>(^1A_g)</td>
<td>2.45</td>
<td>10.0</td>
<td>180</td>
<td>3.48</td>
</tr>
</tbody>
</table>

\(^a R_{e1} = \text{Al}-\text{P}.\)
\(^b R_{e2} = \text{P}-\text{P}.\)
\(^c \theta_{e} = \text{P}-\text{Al}-\text{P} \text{ for Al}_2\text{P}_2 \text{ and Al}_2\text{P}_2^+; \text{Al}-\text{P} \text{ for } 2(\text{AlP}).\)

A critical comparison of the CASSCF and MRSDCI geometry of \(\text{Al}_2\text{P}_2\) reveals that the Al-P side bond lengths shrink by 0.05 Å at the MRSDCI level. The P-Al-P bond angle remains similar at both the CASSCF and MRSDCI levels. We conclude that the geometry of the ground state is not too sensitive to higher-order correlation effects.

An exhaustive study on the \(\text{Ga}_2\text{As}_2^+\) positive ion to be discussed subsequently reveals that \(^2B_{1u}\) is the ground state of the positive ion. For \(\text{Al}_2\text{P}_2^+\) we considered both the \(^2B_{1u}\) and \(^2A_g\) states. Consequently, we rule out these structures as candidates for the ground state of \(\text{Al}_2\text{P}_2^+\).

In Table II, the Al-P bond distances correspond to the four equal sides of the rhombus structure while the P-P bond distance of 2.1 Å is larger than the \(r_e\) of the \(^3\Sigma^+\) ground state of \(\text{P}_2\) (Ref. 50). We expect our computed bond distances to be slightly larger than their true value. The fact that our computed P-P distance in \(\text{Al}_2\text{P}_2\) is only 0.2 Å larger than the diatomic \(\text{P}_2\) which exhibits triple bond between the P atoms, suggests that there is some multiple bonding between the P atoms.

As seen from Table II, the ground state of \(\text{Al}_2\text{P}_2^+\) is a \(^2B_{1u}\) state with Al-P side bond lengths of 2.47 and P-P distance of 2.17 Å at the MRSDCI level of theory. In comparing with the neutral \(\text{Al}_2\text{P}_2\), the \(^2B_{1u}\) state of the positive ion has longer P-P bond lengths but slightly shorter Al-P side bond lengths. The four sides contract up to 0.03 Å; this contraction is compensated by the P-P bond expansion of 0.07 Å. Since the P atom has a considerably higher IP compared to Al, hence we expect most of the ionization to take place on the Al atom. Therefore, we expect the AE \((\text{Al}_2\text{P}_2^+)\) to be less than 8.7 eV if used Raghavachari's 10.7 eV AE for \(\text{Si}_2\). Indeed our computed AE of 8.2 eV supports this argument and hence the computed AE should be at most a few tenths of an eV in error.

### Table III: Equilibrium Geometries and Energies

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Geometry</th>
<th>State</th>
<th>(r_{e1} (\text{Å}))</th>
<th>(r_{e2} (\text{Å}))</th>
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<td>(\text{Ga}_2\text{As}_2)</td>
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</tr>
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</table>

The \(^2A_g\) state of \(\text{Al}_2\text{P}_2^+\) which arises from removal of an electron from a strongly bonding \(3a_g\) orbital is significantly higher in energy since the \(3a_g\) orbital involves P \((3p, \sigma)\) bonding combination. Hence the adiabatic IP is substantially higher. We expect a low-lying \(^2B_{1u}\) state which arises from the removal of an electron from the \(1b_{3u}\) orbital. For \(\text{Al}_2\text{P}_2^+\) this orbital is a bonding combination of \(3p, \sigma\) orbitals of the four atoms perpendicular to the plane of the molecule. This electronic state is definitely above \(^2B_{1u}\) but below the \(^2A_g\) state of \(\text{Al}_2\text{P}_2^+\).

We compute the energy to dissociate \(\text{Al}_2\text{P}_2\) into 2 AlP diatomics, i.e., the energy for the process

\[
\text{Al}_2\text{P}_2 \rightarrow 2\text{AlP}
\]

as 3.48 and 4.03 eV, respectively, at the CASSCF and MRSDCI levels of theory. This value is expected to increase further upon inclusion of quadruple corrections. The \(D_e\) of the \(^3\Sigma^+\) ground state of the diatomic AIP is computed as 2.06 eV (see Table I). Consequently, the atomization energy of \(\text{Al}_2\text{P}_2\) is computed as 8.2 eV. We expect the atomization energy of \(\text{Al}_2\text{P}_2\) to be smaller than \(\text{Si}_2\). Raghavachari\textsuperscript{30} computed the atomization energy of \(\text{Si}_2\) to be 10.7 using a SCF/MP4 method. We note that the \(D_e\) of AIP is only 2.1 eV while the \(D_e\) of \(\text{Si}_2\) is 3.2 eV. This means that \(\text{Al}_2\text{P}_2\) should be bonded by at least 2 eV less than \(\text{Si}_2\) even if \(D_e\) of \(\text{Si}_2\) to yield 2\(\text{Si}_2\) dimers is comparable to \(\text{Al}_2\text{P}_2\). Therefore, we expect the AE \((\text{Al}_2\text{P}_2^+)\) to be less than 8.7 eV if used Raghavachari's 10.7 eV AE for \(\text{Si}_2\). Indeed our computed AE of 8.2 eV supports this argument and hence the computed AE should be at most a few tenths of an eV in error.

### C. \(\text{Ga}_2\text{As}_2^+\) and \(\text{Ga}_2\text{As}_2^+\)

Table III shows the equilibrium geometries and energies of both \(\text{Ga}_2\text{As}_2\) and \(\text{Ga}_2\text{As}_2^+\). As noted before, the previous study\textsuperscript{19} of the \(\text{Ga}_2\text{As}_2\) tetramer revealed that the ground state of this cluster was found to be \(^1A_g\) with a rhombus structure. The equilibrium geometry parameters are shown in Table III for this state. The results of \(\text{Ga}_2\text{As}_2^+\) are new. As evident from Table III, we find that the ground state of \(\text{Ga}_2\text{As}_2^+\) is a \(^2B_{1u}\) state with an equilibrium geometry of a rhombus. The first excited state of the positive ion is \(^2B_{1u}\) with an equilibrium geometry of a rhombus. The first excited state of the positive ion is \(^2D_{1u}\) with an equilibrium geometry of a rhombus.

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\(D_e\) is the electronic ground state of \(\text{Al}_2\text{P}_2\) with an equilibrium geometry of a rhombus.

\(A\text{IP}\) is the ground state of \(\text{Al}_2\text{P}_2\) with an equilibrium geometry of a rhombus.
The 'AZ state has significantly longer Ga-As side bond lengths and As-As diagonal bond lengths. Clearly the highest occupied \( \alpha \) orbital involved in ionization involves the As atoms in the \( ^2A_u \) state and hence this state is quite high in energy.

We compute the \( D_e \) (Ga\(_2\)As\(_2\)) , that is the energy for the process

\[
\text{Ga}_2\text{As}_2 \rightarrow 2\text{GaAs}
\]

as 2.84 and 3.32 eV, respectively, at the CASSCF and MRSDCI levels. Note that the present study is somewhat more accurate as it included an optimized set of active orbitals in the CASSCF compared to the previous study.19 If we take the \( D_e \) of diatomic GaAs as 1.9 eV, then the atomization energy of Ga\(_2\)As\(_2\) is computed as 7.1 eV.

The adiabatic IP of Ga\(_2\)As\(_2\) is computed as 6.90 eV. Since most of the ionization in the \( ^2B_{1u} \) ground state takes place on the group III atom, we are not surprised by the similarity of the IPs of the two species. Note that the experimental IPs of Al and Ga are 6.0 and 5.98 eV, almost the same.50

Meier et al.17 have studied Ga\(_2\)As\(_2\) and Ga\(_3\)As\(_2^+\) among other species. We note that the geometry they obtained for the \( ^4A_g \) ground state of Ga\(_2\)As\(_2\) is nearly the same as the one predicted by Balasubramanian19 before, although Meier et al. have not mentioned this work. We presume that Meier et al. orient Ga\(_2\)As\(_2\) with the xy plane, z axis coinciding with the As atoms. This leads to different irreducible representation labels compared to ours but one can easily reassign these to our orientation. Meier et al. use a SCF/MRDCI method together with a (3s3p1d) and (3s3p2d) basis sets and effective core potentials. Their \( r_e \) (Ga-As) = 2.74 Å and \( r_e \) (As-As) = 2.38 Å are comparable to our values of 2.68 and 2.30 Å, respectively, for these parameters. Their dissociation energy to dissociate Ga\(_2\)As\(_2\) into Ga\(_2\) + As\(_2\) is 2.21 eV compared to a value of 2.5 eV obtained in the previous study19 and a value of 3.32 eV obtained in the present study.

Meier et al. study only the \( ^2B_{2u} \) state (in their orientation) of Ga\(_2\)As\(_2^+\). We note that their \( ^2B_{2u} \) state is equivalent to our \( ^2B_{1u} \) state in our orientation. The adiabatic IP obtained by Meier et al. (6.95 eV) is close to our value of 6.90 eV at the MRSDCI level. However, the geometry obtained by Meier et al. differs from ours. Their \( r_e \) (Ga-As) and \( r_e \) (As-As) values are 2.699 and 2.646 Å, respectively, for the ground state of Ga\(_2\)As\(_2^+\) while our values are \( r_e \) (Ga-As) = 2.62 Å and \( r_e \) (As-As) = 2.43 Å, respectively. The much longer As-As bond length obtained by Meier et al. for this state is contrasted by our As-As bond length which is only 0.13 Å longer than the As-As bond length of the neutral Ga\(_2\)As\(_2\). Since the methods employed by us and Meier et al. are quite comparable, the longer As-As bond length obtained by Meier et al. is somewhat surprising. The comparison made by Meier et al. on GaAs\(_2\) with our previous work does not take into account the corrected parameters in Ref. 4.

Meier et al. compute the atomization energies of Ga\(_2\)As\(_2\) and As\(_2\) as 5.38 and 6.48 eV, respectively. Their AE for Ga\(_2\)As\(_2\) is smaller compared to our value of 7.1 eV. We note that their computed AE of As\(_2\) (6.48 eV) is also below the experimental value of 10.3 ± 0.1 eV reported by Bennett et al.32 This is understandable since electron correlation effects tend to be more important in the computation of the binding energies of group V clusters.

D. \( \text{In}_2\text{Sb}_2 \) and \( \text{In}_2\text{Sb}_2^+ \)

Table IV shows our computed geometries and energy separations of electronic states of \( \text{In}_2\text{Sb}_2 \) and \( \text{In}_2\text{Sb}_2^+ \). As
seen from Table IV, the $^{1}A_g$ ground state of In$_2$Sb$_2$ has 3.10 Å as bond length for the four sides. The Sb–Sb bond length of 2.78 Å is somewhat longer than the diatomic Sb, $r_e$ of 2.34 Å for the $^{2}B_1u$ state. In order to form significant bonding with In atoms, the Sb–Sb bonding will have to be weakened compared to Sb$_2$ which exhibits roughly a triple bond.

The In–Sb bond lengths of the four sides of the rhombus in In$_2$Sb$_2$ are comparable to the diatomic InSb which has a bond length of 3.0 Å in its $^3\Sigma^-$ ground state. Hence, we conclude that the side bonding in In$_2$Sb$_2$ is similar to the In–Sb bonding in the $^3\Sigma^-$ state but the diagonal Sb–Sb bonding is considerably weakened compared to the diatomic Sb$_2$.

Two excited electronic states of $^2B_{1u}$ and $^2A_g$ symmetries were considered for In$_2$Sb$_2^+$. Clearly the $^2B_{1u}$ state is the lowest. A critical comparison of the $^2B_{1u}$ state of In$_2$Sb$_2^+$ with neutral In$_2$Sb$_2$ ($^1A_g$) reveals that the In–Sb bond lengths are a bit shorter but Sb–Sb bond lengths are significantly elongated. This trend is consistent with the $^2B_{1u}$ state of Ga$_2$As$_2^+$. The $^2A_g$ state of In$_2$Sb$_2^+$ is 1.2 eV higher than the $^2B_{1u}$ ground state of In$_2$Sb$_2^+$. At the CASSCF level, the $^2B_{1u} - ^2A_g$ energy separation is 1.47 eV while the corresponding separation of Ga$_2$As$_2^+$ is 1.9 eV. Evidently this energy separation reduces as one goes down the groups. The $^2A_g$ state involves significant lengthening of the four sides of the rhombus structure while the Sb–Sb bond length remains similar to the neutral structure. This is because the $3a_g$ orbital involves strongly both In and Sb orbitals. The removal of an electron from this bonding orbital therefore significantly lengthens the In–Sb bond in the $^2A_g$ state.

The dissociation energy of In$_2$Sb$_2$ to form 2In–Sb molecules, that is the energy for the process,

$$\text{In}_2\text{Sb}_2 \rightarrow 2\text{InSb},$$

is 2.81 eV at the MRSDCI level. The $D_e$ of InSb is 1.35 eV. Hence the atomization energy of In$_2$Sb$_2$ is given by 5.51 eV.

### E. Tl$_2$Bi$_2$ and Tl$_2$Bi$_2^+$

Table V shows the equilibrium geometries and energy separations of the electronic states of Tl$_2$Bi$_2$ and TlBi$_2^+$. The Tl$_2$Bi$_2$ tetramer differs from the lighter analogs in many ways because of relativistic effects.

The Tl–Bi side bond lengths of the $^1A_g$ state with rhombus geometry are similar to the $^3\Sigma^- (0^+)$ diatomic Tl–Bi bond distance but the Bi–Bi distance is 0.41 Å longer than the experimental Bi$_2$ diatomic distance. Of course, the previous study which employs the same Bi RECPs on Bi$_2$ reveals that the Bi–Bi bond distance is theoretically computed.

### TABLE V. Geometries and energy separations for Tl$_2$Bi$_2$ and TlBi$_2^+$.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Geometry</th>
<th>State</th>
<th>CASSCF</th>
<th>MRSDCI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl$_2$Bi$_2$</td>
<td>Rhombus</td>
<td>$^1A_g$</td>
<td>$R_{e1}$ (Å)</td>
<td>$R_{e2}$ (Å)</td>
</tr>
<tr>
<td>Tl$_2$Bi$_2$</td>
<td>$^2B_{1u}$</td>
<td>3.64</td>
<td>2.99</td>
<td>48.5</td>
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<tr>
<td>Tl$_2$Bi$_2$</td>
<td>$^2A_g$</td>
<td>3.91</td>
<td>3.10</td>
<td>46.7</td>
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<tr>
<td>2(TlBi)</td>
<td>Linear</td>
<td>$^1A_g$</td>
<td>3.65</td>
<td>10.0</td>
</tr>
</tbody>
</table>

$^a$ $R_{e1}$ = Tl–Bi.
$^b$ $R_{e2}$ = Bi–Bi.
$^c$ Zero energy is $-14.560$ 089 au. for CASSCI.
$^d$ Zero energy is $-14.746$ 444 au. for MRSDCI.
ed to be 0.1 Å longer than the experimental value. Hence, part of the bond expansion is due to the use of these RECPs in these computations. Even so, the Bi–Bi bond distance in Tl$_2$Bi$_3$ is roughly 0.25–0.3 Å longer than the theoretical diatomic Bi$_2$ distance. Hence the bonding interaction between Tl and Bi atoms substantially overcomes strong interaction between Bi–Bi compared to the diatomic Bi$_2$. Furthermore, relativistic effects significantly destabilize the overall bonding in Tl$_2$Bi$_3$ compared to its lighter analogs. In particular, the bonding interaction of the 6$p_g$ orbitals perpendicular to the plane of the cluster, that is, the $1b_{3u}$ orbital is considerably weaker in Tl$_2$Bi$_3$. Likewise the overall bonding interaction in highest occupied orbitals of other symmetry blocks is also significantly weakened.

The $^2B_{1u}$ ground state of Tl$_2$Bi$_3^+$ exhibits a substantially different behavior due to the above-discussed differences in the orbital interactions compared to the lighter analogs. The $^2B_{1u}$ state exhibits an avoided crossing of two configurations, one with three open shells and the other with a single open shell configuration leading to a substantially different geometry for this state. The dramatic difference between the $^2B_{1u}$ state of Tl$_2$Bi$_3^+$ and their lighter analogs is that the Tl–Bi distance is considerably longer (0.3 Å) compared to the neutral structure while the Bi–Bi distance is very similar to the neutral structure. This is in contrast with the lighter analogs such as In$_2$Sb$_3^+$ and Ga$_2$As$_3^+$ whose $^2B_{1u}$ states exhibit III–V bond lengths similar to the neutral structure and V–V bond distances only 0.07 Å longer than their neutral counterparts. These differences are due to relativistic mass velocity effects which in turn lead to the above mentioned avoided crossing. We will discuss the avoided crossing further in a subsequent section.

The $^4A_g$ state of Tl$_2$Bi$_3^+$, however, exhibits a similar behavior compared to the lighter analogs since the Tl–Bi distances are significantly longer while the Bi–Bi distance is comparable to the neutral structure. This is because the highest occupied $a_g$ orbital of Tl$_2$Bi$_3$ exhibits similar characteristics to the corresponding orbitals of the lighter analogs.

The energy to dissociate Tl$_2$Bi$_3$ into 2TlBi molecules is computed as 1.83 eV. The $D_e$ of TlBi including spin–orbit effects is computed as 0.5 eV. Consequently, the AE of Tl$_2$Bi$_3$ is 2.8 eV which is substantially reduced compared to In$_2$Sb$_3$ due to relativistic effects.

The spin–orbit effects for the $^4A_g$ state of Tl$_2$Bi$_3$ were found to be rather small due to its closed-shell characteristics. The spin orbit contamination with triplet excited states was found to be very small. Hence, the spin–orbit coupling is small at the equilibrium geometry of Tl$_2$Bi$_3$.

IV. THE NATURE OF ELECTRONIC STATES OF TETRAMERS AND THEIR POSITIVE IONS

We note that all tetramers were oriented on the $yz$ plane such that the group V atoms were located on the $y$ axis while the group III atoms were located on the $z$ axis. The labels for the orbitals are in accordance with this orientation. The ground states of all four tetramers require at least two configurations for a satisfactory representation. The leading configuration in our notation is $1a_g^22a_g^23a_g^21b_{1u}^22b_{1u}^21b_{2u}^21b_{3g}^21b_{3u}^2$. The coefficient of the second important configuration, $1a_g^22a_g^23a_g^21b_{1u}^22b_{1u}^21b_{2u}^21b_{3g}^21b_{3u}^2$, increases from 0.18 to 0.27 as one goes down the group. The $2a_g$ and $3a_g$ orbitals have nearly equal occupancies at the CASSCF level (1.952, 1.946). At the CASSCF level, any arbitrary notation of the natural orbitals would yield the same energy. Consequently, the MRCI or CASSCF orbitals do not provide a direct description of the nature of bonding if used separately for interpretation. However, if orbitals with nearly the same occupancies are used together for interpretation, a wealth of insight could be obtained on the nature of bonding.

The overall nature of the orbitals is similar except for Tl$_2$Bi$_2$ for which relativistic effects lead to a different composition as noted below. Figure 1 shows the orbital interaction diagrams for Ga$_2$As$_2$. This interaction picture is similar to Al$_2$P$_2$. The $1a_g$ orbital (not shown in Fig. 1) is predominantly composed of the $(3s_3)$ and $(4s_3)$ orbitals with the same sign as expected. The $2a_g$ and $3a_g$ orbitals are composed of $\alpha_1(3s_1) + \alpha_2(3s_1)$, $\alpha_1(3p_3) - \alpha_2(3p_3)$ although $\alpha(3s_3)$ also makes nonnegligible contributions. The $1b_{1u}$ orbital is composed of $\alpha_1(3p_1) - \alpha_2(3p_1)$ with a small contribution of $\alpha_1(3p_2) + \alpha_2(3p_2)$. The $1b_{3u}$ orbital is primarily $\alpha_1(3s_2) - \alpha_2(3s_2)$ while the $1b_{3g}$ orbital is composed of $\alpha_1(3p_2)$ of all four atoms perpendicular to the plane of the molecule. Note that $\alpha(3p_3) + \alpha(4p_3)$ makes considerably larger contribution than $\alpha(3p_3)$ in the $1b_{1g}$ orbital. Consequently, the shorter P–P diagonal bond is primarily due to the $\alpha(3p_1) + \alpha(3p_2)$ or $\alpha(4p_3) + \alpha(4p_3)$ bonding in the plane perpendicular to the plane of the molecule in the $1b_{3u}$ orbital. The occupancy of the $1b_{1u}$ orbital is 0.107 which arises from the second configuration in which this orbital is occupied.
TABLE VI. Important configurations in the MRCI expansion contributing to some states of Tl,Bi⁺ at R

<table>
<thead>
<tr>
<th>Cluster</th>
<th>State</th>
<th>Coefficient</th>
<th>1a₁</th>
<th>2a₁</th>
<th>3a₁</th>
<th>1b₁u</th>
<th>2b₁u</th>
<th>3b₁u</th>
<th>1b₁u</th>
<th>2b₁u</th>
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<th>2b₁u</th>
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<td>?</td>
<td>?</td>
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</tr>
</tbody>
</table>

The ground state of Al₂P²⁺ is of ²B₁₁u symmetry in our orientation. This state arises from the removal of an electron from the 2b₁₁u orbital. There are three important configurations contributing to the ²B₁₁u state. The second configuration with greater coefficient is analogous to the second CSF of the neutral structure. The third configuration has three open shells (1a₁²2a₂²3a₂²1b₂²2b₂²1b₂²2b₂₁b₃₁b₃₁b₃₁b₃₁).

The ²A₁₁g state of Al₂P₂⁺ arises from removal of an electron from the 3a₁ orbital which is much more strongly bound compared to the 2b₁₁u orbital. Consequently the ²A₁₁g state is considerably higher in energy.

The ground state composition of Ga₂As⁺⁺ is similar to the ground state of Al₂P²⁺. Likewise, we have already discussed the ²A₁₁g state. The ²B₃₁u state is interesting in that it is a strong mixture of six configurations and thus requiring a multiconfiguration SCF treatment. The ²A₁₁u state arises from a three open-shell electronic configuration which involves 3a₁, 2b₁₁u, and 1b₁₁u orbitals.

Since Tl₂Bi⁺ differs from their lighter analogs and is considerably more complex, we show in Table VI the leading contributions contributing to Tl₂Bi⁺. A dramatic difference is noted in the ground state of Tl₂Bi⁺ as seen from Table VI. The ¹A₁₁g, ²A₁₁g, ³A₁₁g, ²B₁₁u, ³B₁₁u configurations undergo an avoided crossing with the ¹A₁₁g, ²A₁₁g, ³A₁₁g, ²B₁₁u, ³B₁₁u configuration thereby making Tl₂Bi⁺ substantially different from its lighter analogs.

The dramatic contrast between Tl₂Bi⁺ and its lighter analogs arises from the substantial relativistic stabilization of the ⁶s orbital of the Tl atom. Consequently the ⁶s² shell does not take part in bonding, a phenomenon known as the inert pair effect. That is the 2a₁ and 1b₁₁u orbitals of Tl₂Bi⁺ become predominantly nonbonding ⁶s² shells on Tl atoms. This leads to a substantially different set composition for other orbitals. Hence the ¹A₁₁g, ²A₁₁g, ³A₁₁g, ²B₁₁u, ³B₁₁u configuration becomes nearly degenerate with the ¹A₁₁g, ²A₁₁g, ³A₁₁g, ²B₁₁u, ³B₁₁u configuration. Therefore Tl-Bi bond distances become much longer in the Tl₂Bi⁺ ²B₁₁u state. We conclude that Tl₂Bi⁺ thus exhibits substantially different behavior compared to its lighter analogs due to relativistic effects.

V. PERIODIC TRENDS

In this section, we compare the geometries, binding energies and ionization potentials of the four tetramers we studied. Figure 2 shows the periodic trend in the rₚ (III–V) distances for both the neutral molecule and the positive ion. Figure 3 shows the equilibrium V–V distance as one goes down the group. Generally, the curve monotonically increases as we go down the group. This is consistent with the increase in atomic radii of the heavier atoms in a given group. However, it is evident from both the figures that Tl₂Bi⁺ and Tl₂Bi⁺⁺ ions deviate substantially from their lighter analogs. As explained before, the origin of this strong deviation in Tl₂Bi⁺ and Tl₂Bi⁺⁺ is the relativistic mass–velocity effect. The crossing of the ionic and neutral curves is
also interesting and it is due to the avoided crossing of configurations for the positive ion.

Figure 4 shows the atomization energies of the four tetramers. The AEs generally decrease as we go down the group but the AE of Tl₂Bi₂ is inclined downwards substantially compared to the lighter analogs. This is due to the relativistic mass–velocity contraction of the outer 6s orbital of Tl which leads to an inert 6s² shell in Tl₂Bi₂. The Al₂P₂–In₂Sb₂ curve is almost collinear suggesting a normal periodic trend and similarity of these species.

Figure 5 shows the ionization potentials of the four tetramers. The IPs of Al, P, and Ga₂As₂ are quite close. This similarity is a consequence of the almost identical IPs of the Al and Ga atoms. However, the IPs of In₂Sb₂ and especially Tl₂Bi₂ are considerably lower.

The experimental IPs⁵⁰ of Al, Ga, In, and Tl atoms are 5.98, 6.0, 5.8, and 6.1 eV. Since most of the ionization takes place on the group III atoms at least for Al₂P₂–In₂Sb₂, the trend in the IPs of these species is consistent with the trend in the IPs of the atoms. The Tl₁Bi₃ molecule is an exception both because of relativistic effects and the above-mentioned avoided crossing. We have already discussed that the ²B₁u state of Tl₁Bi₃⁺ exhibits a dramatically different behavior due to an avoided crossing of two configurations, which in turn arises from relativistic effects.

Overall, all group III–V tetramers considered here exhibit similar properties in that all of them have rhombus ¹A₂ lowest states among the geometries considered. The V–V diagonal bond distances are shorter than the III–V distances as expected. All the positive ions also have the same ground states. A noticeable difference was found in the properties of Tl₁Bi₂ and Tl₁Bi₂⁺ due to relativistic effects and avoided crossings for Tl₁Bi₂⁺.

ACKNOWLEDGMENTS

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42 The major authors of ALCHEMY II are B. Liu, B. Lengsfield, and M. Yoshimine.