THE LOW-LYING ELECTRONIC STATES OF INDIUM TRIMER

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Multi-configuration SCF (MCSCF) followed by multi-reference singles+doubles CI (MRSDCI) calculations which included up to 177000 configurations are carried out on seven low-lying electronic states of indium trimer (\( ^4A_2 \), \( ^4B_1 \), \( ^4B_2 \), \( ^2A_1 \), \( ^2B_2 \) and \( ^4A_1 \)). Two nearly degenerate electronic states of \( ^4A_2 \) and \( ^4B_1 \) symmetries with isosceles triangular geometries are found as the candidates for the ground state. The spin-orbit effects are included through a relativistic configuration interaction method (RCI). The electronic states of \( \text{In}_3 \) are compared with \( \text{Ga}_3 \). The bending potential energy surfaces of seven electronic states of \( \text{In}_3 \) are also obtained. The nature of bondings and potential energy surfaces are analyzed.

1. Introduction

The electronic structural properties of small metal and semi-conductor clusters have been the topics of many investigations in recent years [1–25]. The spectroscopic investigations of small metal clusters have been on the increase due to the advent of supersonic nozzle expansion method, matrix-isolation of clusters and negative ion photodetachment spectroscopic methods. These clusters have a large number of electronic states with varied spatial and spin symmetries and geometries. Thus, their electronic spectra tend to be complex. Theoretical investigations of heavy clusters are quite challenging due to the problem of electron correlation, large relativistic corrections and the existence of very densely packed electronic states for such clusters.

The clusters of GaAs of composition \( \text{Ga}_x\text{As}_y \), InSb of composition \( \text{In}_x\text{Sb}_y \) as well as \( \text{In}_x\text{P}_y^- \) have been generated in recent years using laser vaporization methods [5,17]. Both the \( \text{Ga}_x\text{As}_y \), \( \text{In}_x\text{Sb}_y \) and \( \text{In}_x\text{P}_y^- \) clusters exhibit interesting even-odd alternations and photofragmentation patterns. Duncan and co-workers [18–21] have also examined the photofragmentation patterns of other main group clusters such as \( \text{Sb}_x \) and \( \text{Bi}_x \).

There are no theoretical calculations to date on indium trimer, although in our laboratory the spectroscopic constants and potential energy curves of electronic states of the indium dimer have been obtained [24]. There exists some controversy in the literature on the nature of isoelectronic \( \text{Al}_3 \) cluster. The experimental ESR spectra in the rare gas matrix favor a quartet ground state for \( \text{Al}_3 \) while a recent MCSCF calculation by Basch [15] predicts the ground state to be of \( ^2A_1 \) symmetry. Jet-cooled spectra of \( \text{Al}_3 \) have also been obtained recently [25]. In an earlier investigation, the present authors [12] have examined the electronic states of neutral \( \text{Ga}_3 \) and \( \text{Ga}_3^+ \). These calculations revealed existence of seven low-lying electronic states of \( \text{Ga}_3 \).

Relativistic and spin–orbit effects in addition to electron correlation effects are expected to be large for \( \text{In}_3 \). The general theory and trends of bonding in metallic clusters have been discussed by McAdon and Goddard [26] using generalized valence bond methods. In particular these authors have discussed bonding in \( \text{Li}_3 \), \( \text{Li}_3^- \), \( \text{Ag}_3 \), etc. In this investigation, we carry out complete-active space MCSCF (CASSCF) followed by multireference singles+doubles CI (MRSDCI) calculations on seven electronic states of \( \text{In}_3 \). We also carry out relativistic CI (RCI) calculations using the MRSDCI natural orbitals to compute the spin–orbit effects. The electronic and structural properties of \( \text{In}_3 \) are compared with \( \text{Ga}_3 \). Section 2
describes our method of calculations while section 3 comprises results and discussions.

2. Method of calculations

In an earlier investigation, we have outlined in detail the method of calculations for Ga₃ [12]. In the present investigation, we use a similar method except that both electron correlation effects and spin–orbit effects are taken into account to a higher degree. We oriented the In₃ cluster on the yz plane with the z axis bisecting the In–In–In apex angle of the isosceles triangle. Seven electronic states of different spatial and spin symmetries arising from the ²P ground state of the indium atom are considered. All calculations reported here were carried out in the C₂ᵥ point group. The rationale for choosing seven electronic states is that there are eight possible doublet and quartet states in C₂ᵥ symmetry of which the *A₂ state was found to be much higher for Ga₃.

Relativistic effective core potentials for the indium atom with the outer 5s²5p¹ shell explicitly retained in the valence space are employed in the present calculations. The Gaussian analytical potentials together with the 3s3p Gaussian basis sets were taken from the work of LaJohn et al. [27]. We add to the (3s3p) set a single set of d polarization functions with the exponent 0.212. The error made in the omission of the d¹₀ shell in the valence space should be less than 5% in geometries. In the present investigation, comparison calculations which included the 4d¹⁰ shells in the valence space also were carried out by employing another set of RECPs which included the 4d¹⁰5s²5p¹ in the valence space and the corresponding basis set. The errors in geometries were less than 2%.

MCSCF calculations were carried out to generate the orbitals for the configuration interaction (CI) calculations using the complete active space MCSCF method (CASSCF). In this method the most important electrons (active electrons) are distributed in all possible ways among a chosen set of the most important orbitals called the internal space of orbitals. The four outer 5s and 5p orbitals of each In atom in In₃ correlate into five a₁, four b₂, two b₁, and one a₂ orbitals in the C₂ᵥ group with the molecular orientation defined earlier. A CASSCF calculation which included all the 12 orbitals in the active space with nine electrons distributed in all possible ways generates too large a configuration space for our codes. As we [12] and Basch [15] suggested, the totally symmetric combination of the s orbitals on the metal atoms (1a₁ orbital) does not play a significant role in the CASSCF. Thus in our calculations, the 1a₁ orbital was kept in core in the CASSCF in that excitations were not allowed from the 1a₁ orbital. The fifth a₁ orbital was found to be quite antibonding and somewhat less important in the CASSCF. The seven remaining electrons were distributed in all possible ways among the remaining three a₁, three b₂, two b₁ and one a₂ orbitals in the CASSCF. Although no excitations were allowed from the 1a₁ orbital in the CASSCF, CI calculations included excitations from this orbital.

Configuration interaction (CI) calculations were carried out following CASSCF. The CI calculations were carried out using the multireference singles+double CI (MRSDCI) method. In this method, all those configurations in the CASSCF with coefficients larger than or equal to 0.07 are included as reference configurations. Then single and double excitations were allowed from these reference configurations. Note that excitations from the 1a₁ shell were also included in the MRSDCI. We also calculated the dipole moments and Mulliken populations of all the electronic states of In₃ from the natural orbitals of the MRSDCI calculations.

Spin–orbit effects were included following MRSDCI calculations using the recently developed relativistic CI (RCI) procedure for polyatomics [28]. In this method, low-lying electronic configurations of different spatial and spin symmetries which mix in the presence of the spin–orbit operator (same symmetry in the C₂ᵥ double group) were included as reference configurations. Single and double excitations were allowed from these reference configurations. Spin–orbit integrals were obtained in the same Gaussian basis set using the differences of l+1/2 and l-1/2 relativistic ECPs as the spin–orbit operator. The RCI calculations of the ²A₁,α state, for example, included ²B₂β, ²B₁β, ²A₂α states as reference configurations in addition to configurations of ²A₁,α symmetry and other low-lying states of quartet symmetry. The RCI calculations without the spin–orbit operator were also carried out to find the effect of spin–orbit coupling.

The CASSCF calculations included between 940
and 1525 CSFs depending on the spin multiplicity of the electronic state. The MRSDCI calculations included up to 177000 configurations depending on the electronic state. The CASSCF and MRSDCI calculations were carried out using one of the present authors' modified version of the ALCHEMY II codes \textsuperscript{29}. The Mulliken population analysis was carried out using the modified ALCHEMY property package to exclude the \( d_{x^{2}+y^{2}+z^{2}} \) population from the \( d \) and add it to the \( s \). The spin–orbit integrals were calculated using Pitzer's modified version of ARGOS codes \textsuperscript{30}.

### 3. Results and discussions

#### 3.1. Equilibrium geometries and potential energy surfaces

Table 1 shows the optimized bent equilibrium geometries and their energy separations at both CASSCF and MRSDCI levels of theory. Fig. 1 shows the optimized MRSDCI equilibrium geometries of the electronic states of In\(_{3}\). Fig. 2 shows the actual bending potential energy surfaces for several electronic states obtained using the CASSCF method. As can be seen from table 1, the equilibrium geometries predicted by CASSCF calculations are not substantially different from the MRSDCI geometries. The bond lengths change at the most 0.13 Å. The bond angles change at the most 4\(^{\circ}\) at the MRSDCI level of theory in comparison to the zeroth-order CASSCF level. Table 2 shows the equilibrium geometries and the energy separations of the linear electronic states of In\(_{3}\).

Three nearly degenerate states of quartet symmetry (\( ^{4}A_{2}, ^{4}B_{1}, ^{4}\Sigma^{-}_{u} \)) are possible candidates for the ground state. The MRSDCI calculations predict the \( ^{4}A_{2} \) state to be the lowest, although the \( ^{4}B_{1} \) state is only 0.01 eV above the \( ^{4}A_{2} \) state. The equilibrium geometries of both \( ^{4}A_{2} \) and \( ^{4}B_{1} \) states are isosceles triangles, although \( ^{4}B_{1} \) is very acute. Note that the linear limit of the \( ^{4}A_{2} \left( ^{4}\Sigma^{-}_{u} \right) \) is also only 0.07 eV above the ground state.

The \( ^{2}B_{2} \) state exhibits a very acute geometry and thus the In–In bond lengths for the two-sides of the isosceles triangle are large. As can be seen from fig. 1, both \( ^{2}B_{1} \) and \( ^{2}B_{2} \) states have short In–In bond lengths at the base of the isosceles triangle. Thus, the \( ^{2}B_{1}, ^{2}B_{2}, \) and \( ^{2}A_{1} \) electronic states exhibit enhanced bonding at the base while the other states show greater bond strengths at the equal sides of the isosceles triangles.

The only electronic state with equilateral triangle geometry is the \( ^{4}B_{2} \) state. The \( ^{4}A_{1} \) electronic state has a linear geometry (\( ^{4}\Delta_{g} \)).

Table 3 shows the effect including the 4d\(^{10}\) shells explicitly in the CASSCF calculations on geometries of the low-lying states of In\(_{3}\). As can be seen from this table, the effect of the 4d\(^{10}\) shell on the bond lengths is less than 1.3\% and on the bond angles is less than 0.5\(^{\circ}\) for the three electronic states which we compared. Thus, the 4d\(^{10}\) core electrons do not play an important role in the determination of the geometries of the low-lying states of In\(_{3}\).

### Table 1

Geometries and energies of the bent electronic states of In\(_{3}\)

<table>
<thead>
<tr>
<th>CASSCF</th>
<th>MRSDCI</th>
</tr>
</thead>
<tbody>
<tr>
<td>state</td>
<td>( \theta ) (deg)</td>
</tr>
<tr>
<td>( ^{4}A_{2} )</td>
<td>75.2</td>
</tr>
<tr>
<td>( ^{4}B_{1} )</td>
<td>54.8</td>
</tr>
<tr>
<td>( ^{2}B_{1} )</td>
<td>47.6</td>
</tr>
<tr>
<td>( ^{2}A_{1} )</td>
<td>49.6</td>
</tr>
<tr>
<td>( ^{4}B_{2} )</td>
<td>58.4</td>
</tr>
<tr>
<td>( ^{2}B_{2} )</td>
<td>74.3</td>
</tr>
</tbody>
</table>

\(^{a}\) The two equal sides of the isosceles triangle; \( \theta \)= apex angle.

\(^{b}\) Zero energy for CASSCF is \(-5.513007\) hartree; for MRSDCI is \(-5.609780\) hartree; the zero energy is for the \( ^{4}A_{2} \) ground state at the reported geometry.

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Fig. 1. The equilibrium MRSDCI geometries of eight electronic states of In$_3$. The $^2B_2$ and $^2A_1$ minima correspond to Jahn–Teller components of a $^2E$ state (see section 3.2).

Fig. 2. The bending potential energy surfaces of low-lying states of In$_3$.

Table 2
Properties of the linear electronic states of In$_3$

<table>
<thead>
<tr>
<th>State</th>
<th>CASSCF</th>
<th>MRSDCI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R$ (Å)</td>
<td>$E$ (eV)</td>
</tr>
<tr>
<td>$^2Π_u$</td>
<td>3.07</td>
<td>-0.02</td>
</tr>
<tr>
<td>$^4Σ_u^-$</td>
<td>2.90</td>
<td>0.18</td>
</tr>
<tr>
<td>$^4Δ_g$</td>
<td>3.14</td>
<td>0.73</td>
</tr>
<tr>
<td>$^2Σ_g^+$</td>
<td>2.95</td>
<td>0.87</td>
</tr>
<tr>
<td>$^4Π_u$</td>
<td>2.85</td>
<td>1.29</td>
</tr>
</tbody>
</table>

Table 3
The effect of including 4d$^{10}$ core in the CASSCF calculations of the electronic states of In$_3$

<table>
<thead>
<tr>
<th>State</th>
<th>With 4d$^{10}$</th>
<th>Without 4d$^{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_e$ (Å)</td>
<td>$θ_e$ (deg)</td>
</tr>
<tr>
<td>$^4A_2$</td>
<td>3.01</td>
<td>75.3</td>
</tr>
<tr>
<td>$^2B_1$</td>
<td>3.36</td>
<td>49.1</td>
</tr>
<tr>
<td>$^2A_1$</td>
<td>3.62</td>
<td>49.7</td>
</tr>
</tbody>
</table>

The energy separations of various electronic states are sensitive to higher-order correlations. In fact, the $^2A_1$ and $^4B_2$ states switch order in comparing CASSCF and MRSDCI calculations. The energy separations of most of the excited states increase at the MRSDCI
level of theory implying stabilization of the lowest electronic states.

The atomization energy, i.e. the energy for the following process
\[ \text{In}_3 \rightarrow 3\text{In} \]
was calculated by making a long distance calculations \((R = 8.0 \text{ Å})\) for the linear \(4\text{A}_2\) state. The MRSDCI calculations yield an atomization energy of 48 kcal/mol for \(\text{In}_3\).

Table 4 shows the calculated dipole moments for the electronic states of \(\text{In}_3\) at their equilibrium geometries using the MRSDCI natural orbitals. As can be seen from table 4, all the isosceles triangular structures have large dipole moments. The \(4\text{A}_2\) and \(2\text{B}_2\) states have positive charges at the base atoms while all other isosceles triangular states have positive charges at the apex of the triangle.

Fig. 2 shows the bending potential energy surfaces for the various electronic states of \(\text{In}_3\) obtained using the CASSCF method. The \(4\text{A}_2\) surface contains a bent minimum which correlated into \(4\Sigma_n^\pm\) linear state. The \(4\text{B}_1\) surface is very narrow near \(\theta_e\), goes through a barrier and correlates with the \(4\Delta_g\) linear state. The \(2\text{B}_1\) surface also goes through a much smaller barrier. The crossing of \(4\text{A}_2\) and \(2\text{B}_1\) at \(\theta \approx 140^\circ\) is quite interesting. Note that at the CASSCF level of theory \(2\Pi_u\) state with linear geometry is lower. However, the \(4\text{A}_2\) (bent), \(4\text{B}_1\) (bent), \(2\Pi_u\) (linear), \(2\text{B}_1\) (bent) are all nearly degenerate at this level of theory.

3.2. Nature of low-lying electronic states and bonding

Table 5 shows the coefficients of the most important configurations in the CASSCF wavefunctions of the electronic states of \(\text{In}_3\). The \(1\text{a}_1\) orbital is the totally symmetric linear combination of the 5s orbitals on the three atoms. The \(2\text{a}_1\) orbital is \(-\text{In}_1(5s) + \text{In}_2(5s) + \text{In}_3(5s)\) for the \(4\text{A}_2\) state where \(\text{In}_1\) represents the apex atom of the isosceles triangle. For the \(2\text{A}_1\) state, the \(2\text{a}_1\) orbital is predominantly \(\text{In}_2(5s) + \text{In}_3(5s)\) since the equilibrium geometry of this state is a very acute triangle \((\theta_e \approx 51^\circ)\). The \(3\text{a}_1\) orbital for the \(4\text{A}_2\) state is predominantly made up of the 5s and 5p, and 5p, orbitals of the base atoms. The \(1\text{b}_2\) orbital for the \(4\text{A}_2\) state is predominantly \(\text{In}_2(5s) - \text{In}_3(5s)\) antibonding orbital for both \(4\text{A}_2\) and \(2\text{A}_1\) states. The \(2\text{b}_2\) orbital which is occupied for the \(4\text{A}_2\) state is predominantly \(\text{In}_1(5p) - \text{In}_2(5p) + \text{In}_3(5p)\) bonding orbital. The \(1\text{b}_1\) orbital of \(4\text{A}_2\) state is \(\text{In}(5p) + \text{In}_2(5p) + \text{In}_3(5p)\) bonding orbital in the plane perpendicular to the cluster. This orbital is unoccupied for the \(2\text{A}_1\) state (actual density is 0.05). Hence the \(4\text{A}_2\) state exhibits slight multiple bonding in the plane perpendicular to the trimer while the \(2\text{A}_1\) state is made of in plane bonds. Thus the In–In bond lengths are shorter in the \(4\text{A}_2\) state compared to the \(2\text{A}_1\) state.

Table 6 shows the gross, net and overlap Mulliken populations of the electronic states of \(\text{In}_3\). As can be seen from table 6, the apex atom has a gross population larger than 3.0 for the \(4\text{A}_2\) and \(2\text{B}_2\) states while it is smaller than 3.0 for other states. Thus there is charge transfer in these states except the \(4\text{B}_2\) state which has an equilateral triangular geometry. In general structures with large angle \((\theta_e > 60^\circ)\) equilibrium geometries carry slight negative charges on the central atom while structures with very acute \(\theta_e\) \((\theta_e < 60^\circ)\) carry positive charges on the central atom. This is consistent with the reported dipole moments for these states (table 4). The metal atom s populations are somewhat smaller for all the electronic states. The gross p populations for most of the electronic states are larger than their natural atomic occupations. This seems to suggest some mixing of 5s\(^2\)5p\(^\dagger\) and 5s\(^1\)5p\(^2\) configurations especially in the \(4\text{A}_2\), \(4\text{B}_1\), \(2\text{B}_2\) and \(4\text{A}_1\) states. The d populations are not very large except for the \(4\Sigma_n^\pm\) linear electronic state of \(\text{In}_3\).

Next we discuss differences in bondings and electronic properties of different states for \(\text{In}_3\). We use figs. 1 and 2 and tables 5 and 6 as references of our discussion. As seen from fig. 2, the \(4\text{A}_2\), \(2\text{B}_2\), \(4\Sigma_n^\pm\), \(2\Pi_u\) and \(4\Delta_g\) states form linear or relatively large angle
minima compared to \( ^2A_1 \), \( ^2B_1 \), \( ^4B_1 \), and \( ^4B_2 \) states which form very acute triangle or equilateral triangular minima. These differences in the geometries and the nature of potential energy surfaces may be puzzling. Thus it was decided to analyze these further using overlap populations, electronic configurations, etc.

In general, electronic states which exhibit multiple bonding of the central atom to side atoms tend to form linear structures or large angle structures. The In-In overlap populations of the central atom with corner atoms, as well as the In-In base atoms' overlap for different states seem to provide significant insights and clues to the nature of potential energy surfaces and why some states form very acute angle minima whereas other electronic states form large angle or linear minima.

As seen from table 6, the In-In overlaps of the central-corner atoms are considerably larger for the \( ^4A_2 \) and \( ^4\Sigma^- \) states compared to other doublet and quar-
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The electronic configuration of the linear $4\Sigma$ state is $1\sigma_g^2 2\sigma_u^2 1\pi_u^2 2\pi_u^2 1\pi_g$. Evidently, the occupancy of the $\pi_u$ orbital suggests multiple corner bonds in the linear state (see fig. 1). Thus the $4\Sigma$ state exhibits shorter In-In bond lengths of 2.90 Å.

As the molecule is bent from its linear $4\Sigma$ state, the overlaps of the base atoms increase leading to a structure in which both the side and base overlaps attain optimal values for that state. Consequently, the bent $^1A_1$ state geometry in fig. 1 ($\theta_c \approx 71^\circ$) is most consistent with this qualitative description. The In-In overlap at the base is small ($R(\text{base}) = 3.43$ Å) but compensates for the partially destroyed multiple bonding overlap along the central-corner atoms of the linear structure. The final MRSDCI $^4A_2 - ^4\Sigma^-$ separation is only 0.07 eV, confirming this qualitative description.

The $^3\Pi^\prime$ state correlates into the $^4\Sigma^-$ linear state. The $^2\Pi$ nature of this state suggests occupation of a $2\sigma_u$, antibonding orbital ($2b_2$ in table 5). The antibonding interaction is the largest for the linear structure. Thus bending the molecule is favorable since it reduces the antibonding interaction thereby leading to a bent geometry (see fig. 2). At the bent $^3\Pi$ minimum, the repulsive interaction in the $2\sigma_u(2b_2)$ orbital is minimized.

The $^2A_1$ and $^2B_2$ states could be envisaged as the Jahn–Teller components of a $2\Sigma^+$ equilateral triangular structure. Consequently, the Jahn–Teller distortion splits the $^2E'$ state into the $^2A_1$ component with $\theta_c < 60^\circ$ ($\theta_c = 51^\circ$) and the $^2B_2$ component with $\theta_c > 60^\circ$ ($74.4^\circ$). These two structures are analogues of the two nearly degenerate, $^2A_1$ and $^2B_2$ Jahn–Teller components of Au$_3$ and Ag$_3$ clusters discussed in previous studies from our laboratory [31,32]. The MRSDCI splitting of $^2B_2$ and $^2A_1$ states is only 0.1 eV confirming the Jahn–Teller picture of these two states. If these two states are true Jahn–Teller components, then they must cross at $\theta = 60^\circ$. As seen from fig. 2, the $^2A_1$ and $^2B_2$ curves cross very close to $\theta = 60^\circ$. A small difference is due to the size inconsistency in the treatment of electron correlations in these two states. Furthermore, since $^2B_2$ and $^2A_1$ states are Jahn–Teller components of $^2E'$, the central In atom in the two tet states which form small angle minima. In the case of $^2\Sigma^-$ state linear state, In–In central-corner overlaps are the largest (0.96) since direct overlap of the central atom to the other two atoms is most favored in this orientation. The electronic configuration of the linear $^4\Pi^-$ state is $1\sigma_g^2 2\sigma_u^2 1\pi_u^2 2\pi_u^2 1\pi_g$. Evidently, the occupancy of the $\pi_u$ orbital suggests multiple corner bonds in the linear state (see fig. 1). Thus the $^4\Sigma^-$ state exhibits shorter In-In bond lengths of 2.90 Å.

As the molecule is bent from its linear $^4\Sigma^-$ state, the overlaps of the base atoms increase leading to a structure in which both the side and base overlaps attain optimal values for that state. Consequently, the bent $^1A_1$ state geometry in fig. 1 ($\theta_c \approx 71^\circ$) is most consistent with this qualitative description. The In–In overlap at the base is small ($R(\text{base}) = 3.43$ Å) but compensates for the partially destroyed multiple bonding overlap along the central-corner atoms of the linear structure. The final MRSDCI $^4A_2 - ^4\Sigma^-$ separation is only 0.07 eV, confirming this qualitative description.

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states carries opposite charges. In the case of $^2A_1$, the central atom carries approximately 0.086 charge as derived from gross Mulliken population in Table 3. For the $^2B_2$ state the central atom carries $-0.058$ charge. Note that the dipole moments of $^2A_1$ and $^2B_2$ states are 0.80 and $-0.65 \text{ D}$, respectively (Table 4). Thus the dipole moments of these two states follow an approximate "center of gravity" rule in that the $^2A_1$ state differs more from the ideal equilateral triangular geometry. The ideal $^2E'$ structure would have zero dipole moment. This structure is a cusp in the global potential energy surface.

The $^4B_1$ and $^2B_1$ states exhibit similarities in their equilibrium geometries as seen from Fig. 1. In both these states, there is considerable In-In overlap at the base atoms of the isosceles triangle, thereby bringing the base atoms much closer. This is offset by the smaller In-In overlaps at the side of the isosceles triangle. As seen from Table 6, in $^4B_1$, $^2B_1$ and $^2A_1$ states, the total populations of the two M$_2$ atoms (base) are considerably larger than the central atom. There is clearly multiple bonding along the base atoms in the $^4B_1$ and $^2B_1$ states.

The above discussions evidently reveal that the differences in equilibrium geometries and potential energy surfaces are governed by orbital interactions, metal–metal overlaps, charge transfers and multiple bondings along the base or the sides. If multiple bonding or strong orbital overlap occurs at the base, then the structure tends to be very acute. If multiple bonding occurs at the central–corner atoms, the structure exhibits large angle minima or is linear. The $^2B_2$ and $^2A_1$ states are Jahn–Teller components of the $^2E'$ state. In the $^4B_2$ state there is a perfect balance of base and side overlaps leading to an equilateral triangular structure.

The spin–orbit effects on the electronic states of In$_3$ could be important since the atomic $^2P_{3/2}$–$^2P_{1/2}$ splitting of the indium atom is 2200 cm$^{-1}$ [3]. As noted in section 2 the spin–orbit effects were incorporated using the relativistic CI (RCI) method. First, the effect of the spin–orbit term on the geometry was investigated for two low-lying electronic states. It was found that the $R_e$ and $\theta_e$ values did not change at all ($\Delta R_e=0.00 \text{ \AA}$) by the spin–orbit term. The spin–orbit term made more appreciable contribution to the energy separations. Thus RCI calculations for all the states were carried out at the MRSDCI optimized geometries.

Table 7 shows the effect of spin–orbit coupling on the electronic states of In$_3$. The electronic states are lowered in energy overall by the spin–orbit coupling. However, the splitting between different spin–orbit states for a given electronic state is somewhat small. The spin–orbit stabilization is about 0.01 eV for most of the electronic states. Thus, spin–orbit effects are not very significant for the electronic states of In$_3$.

### 3.3. Comparison of electronic states of In$_3$ with Ga$_3$, and predictions on Tl$_3$

In this section, we compare the electronic states of In$_3$ with its lighter analogue, namely, Ga$_3$. In an earlier investigation, the present authors studied the electronic states of Ga$_3$. The two trimers differ in many ways. For Ga$_3$, the $^2A_1$ state is the ground state while the $^4A_2$ state is about 0.24 eV above the ground state. For In$_3$, however, the $^4A_2$ and $^4B_1$ states are considerably lower in comparison to the $^2A_1$ state. The $^2A_1$ state, in fact, is 0.35 eV above the $^4A_2$ state. For both the species, $^4A_1$ state of linear geometry is the highest in energy. For Ga$_3$, the $^4A_1$ state is 1.38 eV above the ground state while the corresponding state

<table>
<thead>
<tr>
<th>State</th>
<th>$E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4A_2(\alpha\alpha\alpha)$</td>
<td>0.000</td>
</tr>
<tr>
<td>$^4A_2(\alpha\alpha\beta+\beta\alpha+\beta\alpha)$</td>
<td>0.006</td>
</tr>
<tr>
<td>$^4B_2(\alpha\alpha\alpha)$</td>
<td>0.011</td>
</tr>
<tr>
<td>$^4A_2$</td>
<td>0.015</td>
</tr>
<tr>
<td>$^4B_2(\alpha\beta+\beta\alpha+\beta\alpha)$</td>
<td>0.015</td>
</tr>
<tr>
<td>$^4B_2$</td>
<td>0.025</td>
</tr>
<tr>
<td>$^2B_1(\alpha)$</td>
<td>0.121</td>
</tr>
<tr>
<td>$^2B_1$</td>
<td>0.125</td>
</tr>
<tr>
<td>$^4B_2(\alpha\beta+\beta\alpha+\beta\alpha)$</td>
<td>0.360</td>
</tr>
<tr>
<td>$^4B_2(\alpha\alpha\alpha)$</td>
<td>0.361</td>
</tr>
<tr>
<td>$^4B_2$</td>
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</tr>
<tr>
<td>$^2A_1(\alpha)$</td>
<td>0.452</td>
</tr>
<tr>
<td>$^2B_2(\alpha)$</td>
<td>0.456</td>
</tr>
<tr>
<td>$^2A_1$</td>
<td>0.465</td>
</tr>
<tr>
<td>$^2B_2$</td>
<td>0.465</td>
</tr>
<tr>
<td>$^4A_1(\alpha\alpha\alpha)$</td>
<td>0.779</td>
</tr>
<tr>
<td>$^4A_1(\alpha\beta+\beta\alpha+\beta\alpha)$</td>
<td>0.783</td>
</tr>
<tr>
<td>$^4A_1$</td>
<td>0.785</td>
</tr>
</tbody>
</table>
for In$_3$ is only 0.77 eV above the ground state. In general, the seven electronic states are more closely packed for In$_3$ in comparison to Ga$_3$. The metal–metal bond lengths are longer for In$_3$ as expected in comparison to Ga$_3$. The difference in the properties of Ga$_3$ and In$_3$ noted above seems to arise from both relativistic effects and the fact that the atomic energy separations are lower for In in comparison to Ga. For example, the $4P$ state arising from $4s4p^2$ is 38000 cm$^{-1}$ above for Ga while the corresponding state ($5s5p^2$) is 35000 cm$^{-1}$ above the ground state for In [33].

The dramatic difference between the electronic states of Ga$_3$ and In$_3$ is in the ionity of the metal–metal bonding. The dipole moments of the electronic states of In$_3$ are considerably larger in comparison to the corresponding states of Ga$_3$. This trend is expected since the indium atom is more metallic (more electropositive) than gallium atom.

In comparing the Mulliken populations of the electronic states of Ga$_3$ and In$_3$, we note that the metal–metal overlaps are much smaller for In$_3$. This is mainly because the bonding is weaker in In$_3$ in comparison to Ga$_3$. For example, the $M$–$M_2$ overlaps for $^4A_2$ of Ga$_3$ and In$_3$ are 0.931 and 0.686, respectively. The metal $s$ populations are considerably smaller for Ga$_3$ in comparison to In$_3$. This should be mainly due to relativistic mass–velocity stabilization of the $5s^2$ shell of the indium atom in comparison to the $4s^2$ shell of the gallium atom. This is the primary factor for the weakening of the metal–metal bond in the electronic states of In$_3$ in comparison to the electronic states of Ga$_3$. The metal $d$ populations are considerably larger for Ga$_3$ in comparison to In$_3$. The gross $d$ populations of the electronic states of Ga$_3$ are between 0.14 and 0.27 while the corresponding populations for In$_3$ are 0.07–0.09. Thus, the metal $d$ orbital participation is somewhat smaller for In$_3$.

Based on the above comparison of Ga$_3$ and In$_3$, some predictions can be made on the properties of low-lying electronic states of Ti$_3$. In our laboratory, we completed extensive calculations on the potential energy curves of Ga$_2$ [34] and In$_2$ [24], whereas Christiansen and Pitzer [35] completed calculations on the potential energy curves of low-lying states of Ti$_2$. The ground state of Ti$_2$ was found to be a $0_\pi^-$ state arising from a $^3\Pi_u$ state with very small binding energy. The $R_e$ of In$_2$ was found to be 3.14 Å, whereas the $R_e$ of $0_\pi^-$ state of Ti$_2$ is 3.54 Å. The much longer bond length and weaker Ti–Ti bond in Ti$_2$ is mainly due to the inert pair effect which is actually a consequence of the relativistic mass–velocity stabilization of the $6s^2$ shell of Ti. Hence for Ti$_3$, the inert-pair effect and relativistic spin–orbit effects will play a major role in the determination of electronic properties. Based on the theoretical bond lengths for Ti$_2$ and Ga$_2$, we believe that Ti–Ti bond lengths should be about 0.4 Å longer. For example, the $^2B_2$ and $^2A_1$ Jahn–Teller components of Ti$_3$ should still have $\theta_e > 60^\circ$ and $\theta_e < 60^\circ$, respectively. But Ti–Ti bond length in the $^2A_1$ state for the side atoms would be roughly 3.9 Å, while the base bond length would be 3.4 Å, if $\theta_e$ were to be about the same. Similarly, in the $^2B_2$ state Ti–Ti side bond lengths would be 3.5 Å while the base bond length would be 4.1 Å. Those states in which $5s^25p^{1-5}5s5p^2$ mixings were found for In$_3$, would become less favorable for Ti$_3$ due to the operation of the inert pair effect. These predictions are only speculations which are yet to be verified by relativistic calculations of comparable quality.

4. Conclusion

In this investigation, we carried out CASSCF/MRSDCI calculations on seven low-lying electronic states ($^4A_2$, $^4B_1$, $^2B_1$, $^4B_2$, $^2A_1$, $^2B_1$ and $^4A_1$) and their potential energy surfaces for In$_3$. The MRSDCI calculations included up to 177000 configurations. Two nearly degenerate states of $^4A_2$ and $^4B_1$ symmetries with isosceles triangular geometries were found as candidates for the ground state ($^4A_2$: $R_e$ (side) = 2.95 Å, $R_e$ (base) = 3.43 Å; $^4B_1$: $R_e$ (side) = 3.12 Å, $R_e$ (base) = 2.89 Å). The atomization energy of In$_3$ was calculated as 48 kcal/mol at the MRSDCI level of theory. The analyses of bondings, Mulliken populations and dipole moments revealed that orbital overlaps, charge transfers and the leading configurations determine the nature of metal–metal bonds in the low-lying states of In$_3$. The $^2B_2$ and $^2A_1$ states of In$_3$ were interpreted as Jahn–Teller components of a $^2E$ state. Electronic states with $\theta_e > 60^\circ$ were found to carry negative charges on the central atom (positive charges on the side atoms) while states with $\theta_e < 60^\circ$ were found to carry positive charges on the central atom.
The analyses of Mulliken populations revealed 5s25p1–5s15p2 mixing in some of the electronic states. The properties and equilibrium geometries of In3 were compared with Ga3.

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References