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Citation: *The Journal of Chemical Physics* **94**, 6664 (1991); doi: 10.1063/1.460294

View online: <http://dx.doi.org/10.1063/1.460294>

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Electronic states of Ga₄ and In₄

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(Received 27 December 1990; accepted 5 February 1991)

Complete active space–multiconfiguration self-consistent-field (CAS–MCSCF) followed by configuration interaction calculations, which included up to 250 000 configurations, are carried out on 16 electronic states of Ga₄ and In₄. Three nearly-degenerate electronic states of ³B_{3u}, ³A_u, and ¹A_g symmetries with rhombus, square, and square geometries, respectively, are found as candidates for the ground states of Ga₄ and In₄. The tetramers of Ga and In are bound by 1.2 and 1 eV, respectively, compared to the trimers.

I. INTRODUCTION

Geometries, ionization potentials, binding energies, spectroscopic properties, and other properties of main group clusters have been the topic of a large number of theoretical and experimental studies.^{1–30} Specifically, the Group III clusters and other compounds containing B, Al, and Ga, have received considerable attention.^{19–33} While the dimers and trimers of Group III atoms have been studied extensively, this is not the case for the tetramers of Ga and In. As noted in a recent study by Janiak and Hoffmann,²⁰ it is important to have insight into clusters of these atoms to understand the nature of metal–metal interaction in larger clusters and solids containing Tl and In atoms.

The study of Ga_n and In_n clusters are of considerable importance in the thin-film depositions and thin layer growth in the deposition of multilayer structures. The only study on tetramers and larger clusters containing Ga up to now is the molecular dynamics simulation of Ga microclusters.²¹ It was inferred that planar structures in general are more favored for these clusters.

The clusters of GaAs of the composition Ga_xAs_y have been generated by O'Brien *et al.*¹² by laser vaporization of GaAs crystal. These authors observed interesting odd–even alternations in the ionization potentials of the Ga_xAs_y cluster. Further, the relative abundance in the mass spectra of smaller clusters deviated considerably from the expected binomial distributions observed for the larger clusters. It is also interesting to note that while the experimental electronic spin resonance (ESR) spectra³⁴ in the rare gas matrix favor a quartet ground state for Al₃, recent theoretical calculations yielded a ground state of ²A₁ symmetry with a near-equilateral triangular geometry.³²

The objective of the present study is high-level *ab initio* study on several low-lying electronic states of Ga₄ and In₄ based on the complete active space–multiconfiguration self-consistent-field (MCSCF) followed by large-scale configuration interaction (CI) methods. We find three nearly degenerate candidates for the ground states of Ga₄ and In₄, all of which have planar rhombus geometries. We also find that the tetramers of Ga and In are roughly 1.3 and 1 eV more stable than the corresponding trimers.

II. METHOD OF INVESTIGATION

We employ relativistic effective core potentials (RECPs) for the Ga and In atoms with the outer *ns*²*np*¹ shells (*n* = principal quantum number) explicitly retained in the calculations. In an earlier study,²⁶ the results obtained using (*n* – 1)*d*¹⁰*ns*²*np*¹ (13e RECPs) RECPs were compared for In₃ with 3e RECPs. It was found that distances were within ± 0.04 Å and bond angles within 1.5°. A valence Gaussian basis set of the type (3s3p1d) described previously in our studies on Ga₃²⁵ and In₃²⁶ was used in the present study.

Complete active space–multiconfiguration self-consistent-field method (CAS–MCSCF) was used to generate the orbitals for CI calculations. Preliminary CAS–MCSCF computations considered different geometries for the low-lying electronic states considered here such as planar rhombus (including square), tetrahedron, linear, rectangular, etc. Among these planar rhombus structure and its variation, (square) were found to be the lowest. Hence, the rhombus geometry was studied extensively. A cubic multidimensional polynomial fit was used for optimizing geometries.

All final CAS–MCSCF and CI calculations of the rhombus structure were made in the *D*_{2h} group. The outer *ns* and *np* orbitals of the four atoms spanned four *a*_g, three *b*_{2u}, three *b*_{1u}, two *b*_{3g}, two *b*_{3u}, one *b*_{1g}, and one *b*_{2g} representations. Our preliminary calculations revealed that the lowest *a*_g orbital which is composed of the totally symmetric combination of the *ns* orbitals of the Group III atoms is considerably lower in energy. Consequently, no electronic excitations from this orbital were allowed at the CAS–MCSCF level. Furthermore, the *b*_{2g} orbital which is composed of the antisymmetric combination of the *np*_x orbitals of the Ga atoms located along the longer diagonal of the rhombus did not play an important role. Similarly the last *b*_{2u}, *b*_{1g}, *b*_{3g}, and *b*_{3u} orbitals were antibonding combination. Omission of these orbitals resulted in an active space of three *a*_g, two *b*_{2u}, two *b*_{1u}, one *b*_{3g}, and one *b*_{3u} orbitals. Ten outer electrons (note that excitations from 1*a*_g² were not allowed) were distributed in all possible ways among these nine orbitals in the CAS–MCSCF calculations. This resulted in a manageable number of less than 1000 configuration spin functions (CCSFs) at the CAS–MCSCF stage.

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We carried out multireference singles + doubles configuration interaction (MRSDCI) calculations following CAS-MCSCF. All configurations in the CAS-MCSCF with coefficients ≥ 0.09 were included as reference configurations in the MRSDCI. An initial set of MRCI computations were made which did not allow two electrons to be distributed in the external space. The natural orbitals obtained from this calculation were used to truncate the external space into two sets, retaining only those orbitals with larger densities in the first set. In the final calculation, the second set consisted of 26 orbitals. The MRSDCI calculations included excitations of all 12 electrons. Single and double excitations were allowed for these configurations. Our MRSDCI calculations included up to 250 000 CSFs. The MRSDCI calculations were made for all electronic states considered in this study. The CASMCSCF and MRSDCI calculations were carried out using one of the present authors, K.B's³⁵ modified version of the ALCHEMY II codes.³⁶

III. RESULTS AND DISCUSSION

A. Electronic states of Ga₄

Since the ground state of the Ga atom is a 2P state arising from the $4s^24p^1$ configuration, four Ga 2P atoms would together constitute a large array of singlet, triplet, quintet, and heptet electronic states. It is evident that high spin heptet states will not be strongly bound since there is no flexibility for bond pair formation in the high spin states. Previous studies on Ga₃²⁵ also did not yield any bound sextet states. All these considerations eliminate the possibility of low-lying heptet states for Ga₄.

The previous study on Ga₃²⁵ yielded 2A_1 to be the ground state. Three electronic states of 4A_2 , 2B_1 , and 4B_1 states were found to be 0.3 eV above the ground state. Consequently, combination of these states with another Ga(2P) would yield an array of triplet and singlet states. The quintet

states of Ga₄ are not likely candidates for the ground state of Ga₄.

Table I shows the CAS-MCSCF geometries and energy separation of several triplet and singlet electronic states of Ga₄. As seen from Table I at the CAS-MCSCF level, there are three nearly degenerate electronic states with rhombus and nearly square geometries. The small deviation in the bond angles of the square structures for 3A_u and 1A_g states is primarily an artifact of truncation of the active space in the CAS-MCSCF stage of calculations.

At the CAS-MCSCF level, the $^3B_{3u}$ state with a rhombus structure, whose Ga-Ga side length of 2.63 Å, is the lowest. This compares well with the Ga-Ga bond length of 2.51 Å and 2.62 Å for the 1A_1 and 4A_2 electronic states of Ga₃.²⁵

There are five electronic states within 0.5 eV energy separation for Ga₄. Since the accuracy of energy separations obtained by the CAS-MCSCF method cannot be too much smaller than this value, all these states should be considered as candidates for the ground state of Ga₄.

The geometries of some of the triplet and singlet states of the same spatial symmetries are alike as they arise from the same electronic configuration. For example, the $^3B_{3u}$ and $^1B_{3u}$, $^3B_{1g}$ and $^1B_{1g}$, 3A_u and 1A_u , $^3B_{2g}$ and $^1B_{2g}$, $^3B_{1u}$ and $^1B_{1u}$ states have bond angles within 5° of each other and bond lengths within 0.05 Å of each other. Hence, the configurations contributing to the triplet and singlet states of these symmetries are similar. The exception to this is the closed shell 1A_g state.

Table II shows the MRSDCI geometries and energy separations of the electronic states of Ga₄. In comparing Tables I and II, we note that the acute apex angles of the rhombus structures of these states open up due to higher-order correlation effects. Higher-order correlation effects tend to equalize the interactions of two diagonals of the rhombus structure. Hence, structures with geometries near

TABLE I. CASSCF geometries and energy separations of electronic states of Ga₄.

Electronic state	r_e (Å) ^a	θ_e (°) ^b	E (eV)
$^3B_{3u}$	2.63	78	0.0
3A_u	2.66	89	0.09
1A_g	2.74	88	0.18
$^1B_{3u}$	2.63	79	0.39
$^3B_{1g}$	2.76	58	0.46
1A_u	2.68	86	0.66
$^1B_{1g}$	2.76	58	0.67
$^3B_{2g}$	2.76	60	0.82
$^3B_{1u}$	2.87	68	0.92
$^1B_{2g}$	2.75	60	0.99
$^3B_{3g}$	3.09	53	1.03
$^1B_{1u}$	2.82	63	1.19
$^1B_{3g}$	3.06	52	1.23
$^1B_{2u}$	2.88	70	1.55
3A_g	3.41	51	2.50

^a r_e is the Ga-Ga bond length of four equal sides of the rhombus.

^b θ is the acute bond angle of the rhombus.

TABLE II. MRCI geometries and energy separations of Ga₄.

State	r_e (Å) ^a	θ (°) ^b	E (eV)
$^3B_{3u}$	2.65	92	0.0
3A_u	2.67	90	0.03
1A_g	2.74	89	0.08
$^1B_{3u}$	2.67	83	0.24
1A_u	2.70	84	0.48
$^3B_{1g}$	2.77	60	0.56
$^1B_{1g}$	2.77	58	0.80
$^3B_{1u}$	2.87	69	0.87
$^3B_{2g}$	2.78	59	0.92
$^3B_{2u}$	2.90	71	0.95
$^1B_{2g}$	2.76	60	1.05
$^3B_{3g}$	3.06	54	1.05
$^1B_{1u}$	2.83	63	1.30
$^1B_{3g}$	3.08	53	1.39
$^1B_{2u}$	2.88	71	1.62
3A_g	3.34	52	2.60

^a Equal sides of the rhombus.

^b Acute Ga-Ga-Ga bond angle.

square at the CAS-MCSCF level almost attain square geometries as noted for the 3A_u , 1A_g states of Ga₄. This trend is similar to the trend we found for Ga₃. For example, at the CASSCF level, Ga-Ga bond lengths of the sides of the isosceles triangle of Ga₃²⁵ are 2.51 Å ($\theta_e = 62^\circ$) while at the MRCI level these values become 2.58 Å and $\theta_e = 61^\circ$.

The MRSDCI method essentially retains the three nearly degenerate states as candidates for the ground states of Ga₄ ($^3B_{3u}$, 3A_u , and 1A_g). This is not surprising in view of the fact that Ga₃ has four very low-lying states of 2A_1 , 4A_2 , 2B_1 , and 4B_1 symmetries. Similarly, Ga₂ has very low-lying $^3\Pi_u$ and $^3\Sigma_g^-$ states (within 500 cm⁻¹). The near-degeneracy effects found in the smaller gallium clusters is also seen in Ga₄.

Katircioğlu and Erkoç²¹ have investigated the energies and the structural stabilities of Ga_n ($n = 3-7$) using the molecular dynamics method employing two- and three-body interactions modeled by Lennard-Honnes and Axirod-Teller type functions. They find that Ga₄ has a rhombus structure with all four-equal bond lengths (a) being 2.5 Å. The shorter diagonal bond lengths obtained by these authors is 2.56 Å. Our MRCI a and b bond lengths for the $^3B_{3u}$ state are 2.65 and 3.48 Å. Hence, we conclude that the side bond lengths are more reasonably predicted in the molecular dynamics study than the diagonal bond lengths. However, such molecular dynamics studies typically yield only an average of bond lengths of several low-lying states. For example the $^3B_{1g}$ state has identical a and b value of 2.77 Å. Consequently, while molecular dynamics simulations predict a rhombus structure with very acute bond angles, our *ab initio* studies predict rhombus geometries tending towards square structures.

We compute the binding energy of Ga₄ relative to Ga₃ + Ga as 1.4 eV. The atomization energy of Ga₃ was calculated before as 2.32 eV.²⁵ Hence, the atomization energy of Ga₄ is estimated as 3.72 eV. This is expected to be a lower bound and hence we predict that AE

(Ga₄) = 3.9 ± 0.2 eV. Equivalently, the binding energy per atom is ~ 0.97 eV. Our computed values for Ga₄ are in excellent agreement with the AE of 3.834 eV predicted by Katircioğlu and Erkoç.²¹ Although this agreement should be considered fortuitous in view of the differences in the a and b bond lengths obtained by us and Katircioğlu and Erkoç,²¹ this is encouraging.

B. Electronic states of In₄

Table III shows the CAS-MCSCF geometries of the electronic states of In₄ considered in this study. There is considerable similarity in the geometries of In₄ and Ga₄. The Ga-Ga-Ga acute angles of various electronic states of Ga₄ are very comparable to the corresponding electronic states of In₄. For example, the CAS-MCSCF acute angle of the $^3B_{3u}$ states of Ga₄ and In₄ are 78° and 71° , respectively.

The $^3B_{3u}$, 1A_g , and 3A_u states of In₄ are even more closely clustered than in Ga₄. Higher-order electron correlation effects may eventually favor the 1A_g state of In₄ with a square equilibrium geometry.

The In-In bond lengths are considerably longer compared to the Ga-Ga bond lengths. The three lowest electronic states of In₃ are 4A_2 , 4B_1 , and 2B_1 , all of which have isosceles triangular geometries. The In-In bond lengths of the isosceles triangle of these three states are 2.95, 3.12, and 3.31 Å. The longer sides of the 2B_1 state are understandable since the 2B_1 state forms a very acute triangular geometry. Thus the In-In side bond lengths of the rhombus structures of the $^3B_{3u}$, 1A_g , and 3A_u states are closer to the In-In side bond lengths of 4A_2 and 4B_1 states of In₃.

Table IV shows the MRSDCI geometries and energy separations for In₄. The geometry changes induced by higher-order electron correlation effects for In₄ are akin to Ga₄. In general, the acute In-In-In bond angles open up. Structures which are close to square geometry become almost perfect squares. At the final MRSDCI level we find three elec-

TABLE III. CASSCF geometries and energy separations of In₄.

State	r_c (Å) ^a	θ_c (°) ^b	E (eV)
$^3B_{1u}$	2.98	77	0.0
1A_g	3.10	90	0.02
3A_u	3.02	86	0.07
$^3B_{1g}$	3.12	58	0.31
$^1B_{3u}$	2.98	78	0.35
1A_u	3.03	90	0.43
$^3B_{1u}$	3.22	69	0.51
$^1B_{1g}$	3.12	58	0.51
$^3B_{2u}$	3.27	69	0.60
$^3B_{2g}$	3.12	60	0.63
$^3B_{3g}$	3.45	54	0.67
$^1B_{2g}$	3.11	61	0.79
$^1B_{1u}$	3.18	63	0.86
$^1B_{3g}$	3.41	53	0.87
$^1B_{2u}$	3.23	70	1.19
3A_g	3.73	53	1.93

^a Equal sides of the rhombus.

^b Acute In-In-In bond angle.

TABLE IV. MRSDCI geometries and energy separations of electronic states of In₄.

State	r_c (Å) ^a	θ (°) ^b	E (eV)
$^3B_{1u}$	3.00	83	0.0
1A_g	3.07	90	0.04
3A_u	3.09	90	0.06
1A_u	3.02	90	0.36
$^3B_{1g}$	3.12	60	0.42
$^1B_{1u}$	3.20	68	0.58
$^1B_{1g}$	3.11	60	0.68
$^3B_{2u}$	3.23	71	0.69
$^3B_{2g}$	3.10	60	0.70
$^3B_{3g}$	3.38	55	0.80
$^1B_{2g}$	3.09	60	0.95
$^1B_{1u}$	3.17	63	1.02
$^1B_{3g}$	3.43	54	1.08
$^1B_{2u}$	3.20	71	1.33
3A_g	3.64	53	2.09

^a Equal sides of the rhombus.

^b Acute In-In-In bond angle.

tronic states of ${}^3B_{3u}$, 1A_g , and 3A_u symmetries, two of which have perfect square geometries. Because of its closed-shell character, the 1A_g state retains a square geometry. Hence, we conclude that the ground state of In₄ cannot be established unambiguously, but there are three probable candidates with planar square or rhombus geometries.

The energy required to remove an In atom from In₄ is computed as 1 eV. In a previous study the atomization energy of In₃ was computed as 2.1 eV.²⁶ Consequently, a lower bound for the *AE* (In₄) is established as 3.1 eV. We consider this as a lower bound since higher-order electron correlation effects and basis set improvements would increase the *AE*.

On the other hand, the spin-orbit coupling changes the symmetry of the Hamiltonian, thereby causing the ${}^3B_{1g}$ (A_g) state to mix with 1A_g (A_g) for In₄. The other electronic states compatible with 1A_g (A_g) are the ${}^3B_{2g}$ (A_g) and ${}^3B_{3g}$ (A_g) states lying 0.7–0.8 eV above the ground state. The spin-orbit coupling of the closed shell 1A_g state with open shell states is likely to be small. But the atomic ${}^2P_{3/2}$ – ${}^2P_{1/2}$ separation is 2200 cm^{−1}, which suggests that the ${}^2P_{1/2}$ state is stabilized relative to 2P by 1460 cm^{−1}. Hence, the In₄ cluster will be destabilized by spin-orbit coupling. This destabilization is estimated as 0.3 eV. Hence, the spin-orbit corrected *AE* of In₄ is 2.8 ± 0.5 eV.

TABLE V. CASSCF–CI wave functions of electronic states of Ga₄.

Coefficient	$1a_g$	$2a_g$	$3a_g$	$4a_g$	$1b_{2u}$	$2b_{2u}$	$1b_{1u}$	$2b_{1u}$	$1b_{3g}$	$1b_{3u}$
					${}^3B_{3u}$					
−0.943	2	2	1	0	2	0	2	0	2	1
0.152	2	0	1	0	2	0	2	2	2	1
					3A_u					
−0.920	2	2	2	0	2	0	2	0	1	1
−0.205	2	2	0	0	2	0	2	2	1	1
					1A_g					
−0.917	2	2	2	0	2	0	2	0	2	0
−0.197	2	2	0	0	2	0	2	2	2	0
					${}^1B_{3u}$					
−0.939	2	2	1	0	2	0	2	0	2	1
0.172	2	0	1	0	2	0	2	2	2	1
					${}^3B_{1g}$					
0.911	2	2	1	0	2	0	2	1	1	1
0.151	2	2	1	0	1	1	2	1	1	1
					1A_u					
−0.945	2	2	2	0	2	0	2	0	1	1
0.216	2	2	0	0	2	0	2	2	1	1
					${}^1B_{1g}$					
0.940	2	2	1	0	2	0	2	1	1	1
0.152	2	2	1	0	1	1	2	1	1	1
					${}^3B_{2g}$					
0.946	2	2	0	0	2	0	2	1	2	1
−0.139	2	2	0	0	2	2	2	1	0	1
					${}^3B_{1u}$					
−0.954	2	2	1	0	2	0	2	1	2	0
0.153	2	2	1	0	2	2	2	1	0	0
					${}^3B_{3u}$					
−0.952	2	2	2	0	2	0	2	1	1	0
0.148	2	2	0	0	2	2	2	1	1	0
					${}^1B_{2g}$					
0.938	2	2	0	0	2	0	2	1	2	1
−0.167	2	2	0	0	2	2	2	1	0	1
					${}^3B_{3g}$					
−0.956	2	2	1	0	2	0	2	2	1	0
					${}^1B_{1u}$					
0.944	2	2	1	0	2	0	2	1	2	0
−0.145	2	2	1	0	2	2	2	1	0	0
					${}^1B_{3g}$					
−0.952	2	2	1	0	2	0	2	2	1	0
0.166	2	2	1	0	1	1	2	2	1	0
					${}^1B_{2u}$					
−0.935	2	2	2	0	2	0	2	1	1	0
0.146	2	2	0	0	2	2	2	1	1	0
					3A_g					
0.96	2	2	1	0	2	1	2	1	1	0

TABLE VI. CASSCF–CI wave function of electronic states of In₄.

Coefficient	1a _g	2a _g	3a _g	4a _g	1b _{2u}	2b _{2u}	1b _{1u}	2b _{1u}	1b _{3g}	1b _{3u}
					³ B _{3u}					
0.942	2	2	1	0	2	0	2	0	2	1
					¹ A _g					
0.909	2	2	2	0	2	0	2	0	2	0
−0.211	2	2	0	0	2	0	2	2	2	0
					³ A _u					
−0.912	2	2	2	0	2	0	2	0	1	1
0.230	2	2	0	0	2	0	2	2	1	1
					³ B _{1g}					
0.959	2	2	1	0	2	0	2	1	1	1
					¹ B _{3u}					
−0.938	2	2	1	0	2	0	2	0	2	1
					¹ A _u					
−0.910	2	2	2	0	2	0	2	0	1	1
0.179	2	2	0	0	2	0	2	2	1	1
0.179	2	2	0	0	2	2	2	0	1	1
					³ B _{1u}					
−0.955	2	2	1	0	2	0	2	1	2	0
					¹ B _{1g}					
0.940	2	2	1	0	2	0	2	1	1	1
0.151	2	2	1	0	1	1	2	1	1	1
					³ B _{2u}					
−0.941	2	2	2	0	2	0	2	1	1	0
0.198	2	2	0	0	2	2	2	1	1	0
					³ B _{2g}					
0.941	2	2	0	0	2	0	2	1	2	1
−0.165	2	2	0	0	2	2	2	1	0	1
					³ B _{3g}					
−0.956	2	2	1	0	2	0	2	2	1	0
					¹ B _{2g}					
−0.942	2	2	0	0	2	0	2	1	2	1
−0.172	2	1	1	0	2	0	2	1	2	1
					¹ B _{1u}					
−0.945	2	2	1	0	2	0	2	1	2	0
					¹ B _{3g}					
0.951	2	2	1	0	2	0	2	2	1	0
0.168	2	2	1	0	1	1	2	2	1	0
					¹ B _{2u}					
−0.932	2	2	2	0	2	0	2	1	1	0
0.164	2	2	0	0	2	2	2	1	1	0
					³ A _g					
0.895	2	2	1	0	2	1	2	1	1	0
0.409	2	1	1	1	2	1	2	1	1	0

C. Nature of electronic states of Ga₄ and In₄

Tables V and VI show the leading configurations in the CASSCF–CI wave functions of the electronic states of Ga₄ and In₄, respectively. As seen from these tables, almost all electronic states require at least two configurations to be described adequately. The coefficients of the leading configurations for all states of Ga₄ are greater than 0.90 while for In₄ this is true with the exception of the ³A_g state. As seen from Tables V and VI, the ³B_{3u} state is dominated by the 1a_g²2a_g²3a_g1b_{2u}²1b_{1u}²1b_{3g}²1b_{3u} configuration while the ³A_u and ¹A_g states are predominantly described by the 1a_g²2a_g²3a_g²1b_{2u}²1b_{1u}²1b_{3g}²1b_{3u} and 1a_g²2a_g²3a_g²1b_{2u}²1b_{1u}²1b_{3g}² configurations, respectively.

The 1a_g orbital is predominantly Ga₁(4s) + Ga₂(4s) + Ga₃(4s) + Ga₄(4s) orbital, where Ga₁ and

Ga₄ are the Ga atoms located on the z axis while Ga₂ and Ga₃ are the Ga atoms located on the y axis. The 2a_g orbital is composed of Ga₁(4s) − Ga₂(4s) − Ga₃(4s) + Ga₄(4s). The singly occupied 3a_g orbital in the ³B_{3u} state is Ga₁(4p_z) − Ga₂(4p_y) + Ga₃(4p_y) − Ga₄(4p_z). The highest occupied 3a_g orbital is thus a bonding combination composed of the 4p_z orbitals located on the (Ga₁, Ga₄) atoms and the 4p_y orbitals of (Ga₂, Ga₃) atoms.

The 1b_{2u} orbital is predominately Ga₂(4s) − Ga₃(4s), but the mixing with −Ga₁(4p_y) − Ga₂(4p_y) is non-negligible. Hence, there is bonding interaction between Ga₁(4p_y) and Ga₂(4s) as well as Ga₄(4p_y) and Ga₃(4s). Consequently, the near degeneracy of the 4s and 4p orbitals is manifested in the 1b_{2u} orbital of Ga₄. The 1b_{1u} orbital is composed of −Ga₁(4s) − Ga₂(4p_z) − Ga₃(4p_z) + Ga₄(4s). Again, although this orbital is predominantly composed of the 4s orbitals of the Ga atoms located on the z axis, the

mixing of $4p_z$ orbitals located on the Ga atoms placed on the y axis is non-negligible.

The $1b_{3g}$ orbital is composed of $Ga_1(4p_y) - Ga_2(4p_z) + Ga_3(4p_z) - Ga_4(4p_z)$. Note that this results in Ga–Ga bonding interaction along the sides of the rhombus. The $1b_{3u}$ orbital is simply $Ga_1(4p_x) + Ga_2(4p_x) + Ga_3(4p_x) + Ga_4(4p_x)$. Hence, this represents perpendicular π -bonding interaction.

As seen from Table V in the $^3B_{3u}$ state, the $3a_g$ and $1b_{3u}$ (π orbital) orbitals are singly occupied, while in the 3A_u state, the $1b_{3g}$ and $1b_{3u}$ orbitals are singly occupied. The near degeneracy of the two states is explained by the near degeneracy of the $3a_g$ and $1b_{3g}$ orbitals. The $3a_g$ orbital has enhanced bonding along the diagonals, while the $1b_{3g}$ orbital has enhanced bonding along the sides. Hence, the $^3B_{3u}$ state has slightly shorter bond lengths along the sides compared to the 3A_u state.

The difference between the 1A_g and ($^3B_{3u}$, 3A_u) pair of states is in the composition of the $3a_g$ orbital which is doubly occupied in the 1A_g state, while it is singly occupied in the $^3B_{3u}$ and 3A_u states. The contribution of the $-Ga_1(4p_y) - Ga_4(4p_y)$ orbital is significantly enhanced in the $3a_g$ orbital. Note that the $1b_{3u}$ orbital (π_x orbital) is unoccupied in the 1A_g state. Hence, the in-plane bonding in the 1A_g state is enhanced.

The bonding in In₄ is qualitatively similar to Ga₄. The occupancy of the $3a_g$ orbital in the 1A_g state is a bit smaller (1.77) in In₄ compared to Ga₄ (1.82). The ratio of Ga–Ga to In–In Mulliken overlap populations was approximately 2–2.5, suggesting weaker In–In bond strength. This is consistent with significantly longer In–In bond.

IV. CONCLUSION

The CASSCF/MRCI calculations of 16 electronic states of Ga₄ and In₄ reveal three nearly degenerate electronic states of $^3B_{3u}$, 3A_u , and 1A_g symmetries, all of which have planar rhombus and near-square geometries. The atomization energies of Ga₄ and In₄ were computed as 3.9 ± 0.2 and 2.8 ± 0.5 eV, respectively. The analysis of MOs of the three lowest states reveals that the $^3B_{3u}$ and 3A_u states have singly occupied the $1b_{3u}$ orbital exhibiting π bonding perpendicular to the plane, while the 1A_g state exhibits enhanced in-plane bonding.

ACKNOWLEDGMENTS

This research was supported in part by the U.S. National Science Foundation Grant No. CHE-8818869. P.Y.F. thanks Shanghai Metallurgy Institute, Academia Sinica, P. R. China for providing a leave of absence.

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