

# Theoretical investigation of the ground and low-lying excited states of gallium and indium silicides, GaSi and InSi

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The electronic structure and the bonding of 13 electronic states of the diatomic gallium silicide (GaSi) and indium silicide (InSi) have been studied by multireference configuration interaction and coupled clusters methods in conjunction with the basis set (aug-)cc-pwCVQZ(-PP). Potential energy curves have been constructed for all states. Binding energies, spectroscopic parameters, and dipole moments have been calculated. Moreover, the bonding in the different states is analyzed. The potential energy curves of the two molecules, GaSi and InSi, are similar. The binding energies and the bond distances of the ground states of the molecules,  $X^4\Sigma^-$ , are  $D_e=56.2$  kcal/mol (GaSi) and 51.9 kcal/mol (InSi) and  $R_e=2.406$  Å (GaSi) and 2.603 Å (InSi). The first excited state  $a^2\Sigma^-$  is calculated at 17 kcal/mol above the ground state in both molecules. © 2009 American Institute of Physics. [doi:10.1063/1.3271244]

## I. INTRODUCTION

In recent decades, the adsorption and diffusion of group IIIA (B, Al, Ga, and In) metals on the Si surfaces have attracted the attention of the scientific community due to their technological importance for potential applications for atomic-scale devices, as catalysts, and for low-cost mass production of group IIIA-based devices.<sup>1</sup> There are many experimental and theoretical studies on the adsorption of group IIIA metals on the Si surfaces, concerning the geometric and electronic structures, the surface changes associated with metal diffusion on the surface, the growth of group IIIA films on Si, and the properties induced by the adsorption of M on the Si surface.<sup>2</sup> However, as far as we know, there is no published information on the diatomic systems GaSi and InSi, while both the isovalent diatomic BSi (Refs. 3–6) and AlSi (Refs. 5–10) have been studied theoretically and experimentally. The present study is designed to correct for this lack of information on GaSi and InSi, considering that the diatomic MSi, M=B, Al, Ga, and In, are the simplest “building blocks” of the epitaxy of group IIIA films on the Si surfaces. In the course of our previous work on MN, adsorbed at Si(111), for M=B, Al, Ga, and In, it became evident that there was a need for a good description of the diatomic building block, MSi.<sup>11</sup>

The diatomic molecules, GaSi and InSi, are calculated in the present work by multireference configuration interaction<sup>12</sup> (MRCI) and coupled clusters<sup>12</sup> [RCCSD(T)] methods. For all electronic states examined, we report on potential energy curves (PECs), binding energies, spectroscopic parameters, and dipole moments. Moreover, the bonding in the different states is analyzed. Finally, we estimate the oscillator strengths, the A Einstein coefficients, and the corresponding radiative lifetimes for some of the states. As

will be discussed in the following sections, only recently have basis sets been developed, appropriate for a reasonably accurate description of electronic states of molecules involving Ga and In, where the correlation of the d electrons can significantly affect the calculated results. This may also explain the lack of previous theoretical work on these two systems.

In Sec. II we define the computational approach followed, in Sec. III we discuss our results, and in Sec. IV we recapitulate our findings.

## II. BASIS SETS AND METHODS

For the Si atom, the correlation consistent basis sets of Dunning,<sup>13</sup> cc-pVQZ, (16s11p3d2f1g) → [6s5p4d3f2g1h] and aug-cc-pVQZ (17s12p4d3f2g) → [7s6p5d4f3g2h], were used. For the Ga and In atoms, Peterson's<sup>14</sup> correlation consistentlike weighted core basis sets, i.e., cc-pwCVQZ-PP,<sup>15</sup> (17s14p15d5f3g1h) → [8s7p7d5f3g1h], were chosen. The latter employs accurate small-core relativistic pseudopotentials and treats the  $3s^23p^63d^{10}4s^24p^1$  ( $4s^24p^64d^{10}5s^25p^1$ ) electrons of the Ga(In) atom in the *ab initio* calculation. They were developed for 3d4s4p (4d5s5p) correlation and, as shown before, accurate results can be obtained not only with the inclusion of the 3d (4d) electrons of Ga (In) in the correlation space<sup>16,17</sup> but also with the use of an appropriate basis set developed specifically for the 3d (4d) correlation.<sup>16,18</sup>

Next, the above basis sets were augmented with the diffuse functions of the aug-cc-pVQZ basis sets of the Ga and In atoms,<sup>14</sup> and the resulting size of the basis set aug-cc-pwCVQZ-PP is (18s15p16d6f4g1h) → [9s8p8d6f4g1h]. Thus, the contracted basis sets employed, [8s7p7d5f3g1h]<sub>Ga,In</sub> [6s5p4d3f2g1h]<sub>Si</sub> (≡ CQZ-PP) and [9s8p8d6f4g1h]<sub>Ga,In</sub> [7s6p5d4f3g2h]<sub>Si</sub> (≡ ACQZ-PP), consist of a total of 196 (CQZ-PP) and 246 (ACQZ-PP) spherical Gaussian-type one electron functions.

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TABLE I. MRCI(+Q)/aug-cc-pwCVQZ-PP<sub>Ga,In</sub>, aug-cc-pVQZ<sub>Si</sub> atomic separation energies (in eV) of Ga, In, and Si atoms.

Method	Ga		In		Si		
	$^2S \leftarrow a^2P$	$b^2P \leftarrow a^2P$	$^2S \leftarrow a^2P$	$b^2P \leftarrow a^2P$	$^1D \leftarrow ^3P$	$^1S \leftarrow ^3P$	$^5S \leftarrow ^3P$
MRCI	2.908	3.894	2.720	3.620	0.772	1.883	3.861
MRCI+Q	2.989	3.998	2.779	3.703	0.726	1.878	3.958
Expt. <sup>a</sup>	3.005	4.038	2.839	3.787	0.762	1.890	4.113

<sup>a</sup>Reference 24,  $M_J$ —averaged experimental value.

The MRCI method was employed for the present theoretical study. At first, a complete active space self-consistent field (CASSCF) calculation was carried out by allotting the seven “valence” electrons to eight valence orbitals (one  $4s(5s)[3s]$ +three  $4p(5p)[3p]$  on Ga(In)[Si]). However, at the MRCI level the Ga(In)  $3d^{10}(4d^{10})$  electrons were also included in the correlation space. Thus, the  $3d^{10}4s^24p^1$  ( $4d^{10}5s^25p^1$ ) electrons of the Ga (In) atom and the  $3s^23p^2$  electrons of Si were correlated. The MRCI spaces range from  $88 \times 10^6$  ( $^2\Pi$ ) to  $521 \times 10^6$  ( $^2\Delta$ ) CFs. By applying the internal contraction approximation,<sup>19</sup> the size of the CI spaces is reduced by more than an order of magnitude, thus making the computations tractable.

The restricted coupled cluster+ singles+doubles +perturbative triples [RCCSD(T)] single reference method was also employed for the  $X^4\Sigma^-$  and  $1^2\Pi$  states to confirm the MRCI results. In all RCCSD(T), the  $3s^23p^2$  electrons of Si and the  $3d^{10}4s^24p^1$  ( $4d^{10}5s^25p^1$ ) electrons of the Ga (In) atom were correlated. In order to evaluate our RCCSD(T), which is a single reference method, we checked the single ( $t_1$ ) and the double ( $t_2$ ) amplitudes<sup>12</sup> and the  $T_1$  diagnostic because large amplitudes<sup>20</sup> and the  $T_1$  diagnostic<sup>21</sup> usually can be thought of as an indicator of a multireference state. We found that in all calculations of the present work the  $t_1$  and  $t_2$  amplitudes were very small. In most cases, they were smaller than 0.05. Only in a few calculations on the  $1^2\Pi$  state the largest  $t_2$  was about 0.1. Moreover, the  $T_1$  diagnostic is about 0.02 or less in all calculations. These small values of  $t_1$  and  $t_2$  amplitudes and  $T_1$  diagnostic indicate that the single reference RCCSD(T) method is an appropriate method for the calculated states.<sup>20,21</sup>

All calculations were done under  $C_{2v}$  symmetry constraints; however, the CASSCF wave functions possess correct angular momentum symmetry, i.e.,  $|A|=0$  ( $\Sigma^\pm$ ), 1 ( $\Pi$ ), 2 ( $\Delta$ ). This means that  $\Pi$  states are linear combinations of  $B_1$  and  $B_2$  symmetries,  $\Delta$  combinations of  $A_1$  and  $A_2$  symmetries, whereas  $\Sigma^+$  and  $\Sigma^-$  correspond to  $A_1$  and  $A_2$  species, respectively. Of course, MRCI wavefunctions do not display, in general, pure spatial angular momentum symmetry, but  $A_1$  corresponds to  $\Sigma^+$  or  $\Delta$ ,  $A_2$  to  $\Sigma^-$  or  $\Delta$ , and  $B_1$  (or  $B_2$ ) to  $\Pi$  states.

Finally, due to the relatively large number of correlated electrons (17), we encountered significant size nonextensivity effects: on the average, about  $18 mE_h$  at the MRCI level which reduces to about  $7 mE_h$  by including the Davidson correction<sup>22</sup> for unlinked clusters. Only for the  $^6\Pi$  state, the size nonextensivity effects are smaller, namely,  $9(3) mE_h$  at the MRCI(MRCI+Q) level of theory.

All calculations were carried out with the MOLPRO (Ref. 23) suite of codes.

### III. RESULTS AND DISCUSSION

Table I records the energy separation at MRCI(+Q)/aug-cc-pVQZ<sub>Si</sub> aug-cc-pwCVQZ-PP<sub>Ga,In</sub> ( $\equiv$  ACQZ-PP) level of theory of the first four states of the Si atom and the first three states of the Ga and In atoms. As can be seen, the values are in very good agreement with the experimental transition energies.<sup>24</sup>

The ground states of Ga/In( $^2P$ ) and Si( $^3P$ ) give rise to a total of 12 molecular GaSi (InSi)  $^{2S+1}\Lambda$  states, namely,  $^{2S+1}(\Delta[1], \Pi[2], \Sigma[3])$  with  $2S+1=2$  and 4. All 12 states have been calculated here as well as the lowest sextet which correlates with Ga/In( $^2P$ ) and Si( $^5S$ ).

Table II (for electronic states of GaSi) and III (for electronic states of InSi) list the total energies (E) at the potential energy minimum, equilibrium distances ( $R_e$ ), dissociation energies ( $D_e$ ) with respect to the ground state atoms, Mulliken charges on M ( $q_M$ ), spectroscopic parameters (harmonic frequencies and anharmonic corrections  $\omega_e$ ,  $\omega_e x_e$ , rotational vibrational couplings  $\alpha_e$ , and centrifugal distortions  $\bar{D}_e$ ), dipole moments ( $\mu$ ), and energy gaps ( $T_e$ ) at the MRCI, MRCI+Q, and RCCSD(T) levels of theory. Table IV presents the atomic Mulliken populations for the  $4s4p(5s5p)[3s3p]$  orbitals of Ga(In)[Si] atoms and leading configurations of the calculated bound states of GaSi and InSi. In the MRCI leading configurations, the molecular  $\sigma$ ,  $\pi$ , and  $\delta$  orbitals are referred to as the correlated  $3d^{10}4s^24p^1(4d^{10}5s^25p^1)[3s^23p^2]$  electrons of the Ga(In)[Si] atoms. Figures 1 and 2 display the PECs of the 13 states calculated at the MRCI/CQZ-PP and the atomic limits are given in their insets. Figure 3 shows the relative energies of the molecular states of the MSi molecules, M=B, Al, Ga, and In. The data for the BSi (Ref. 3) and AlSi (Ref. 9) molecules were calculated previously by Ornellas and Iwata at the MRCI/cc-pVQZ level of theory. In what follows, we analyze the states of both GaSi and InSi molecules in groups according to their relative energy ordering.

#### A. $X^4\Sigma^-$

As was also reported for the BSi (Refs. 3, 5, and 6) and AlSi (Refs. 5–10) molecules, the ground states of GaSi and InSi are of  $^4\Sigma^-$  symmetry. The  $X^4\Sigma^-$  states correlate with the ground state atoms Ga/In( $^2P$ ;  $M=0$ ) + Si( $^3P$ ;  $M=0$ ), maintaining this character at all internuclear distances calculated.

TABLE II. Absolute energies  $E$  (hartrees), bond lengths  $R_e$  (Å), binding energies  $D_e$  (kcal/mol), harmonic frequencies and anharmonic corrections  $\omega_e$ ,  $\omega_e x_e$  ( $\text{cm}^{-1}$ ), rotational vibrational couplings  $\alpha_e$  ( $\text{cm}^{-1}$ ), centrifugal distortions  $\bar{D}_e$  ( $\text{cm}^{-1}$ ), Mulliken charges on the gallium  $q_{\text{Ga}}$ , dipole moments  $\mu$  (debye), and energy differences  $T_e$  (kcal/mol) of the gallium silicide, GaSi, at MRCI, MRCI+Q, and RCCSD(T)/cc-pwCVQZ-PP<sub>Ga</sub> cc-pVQZ<sub>Si</sub> (CQZ-PP) and aug-cc-pwCVQZ-PP<sub>Ga</sub> aug-cc-pVQZ<sub>Si</sub> (ACQZ-PP) levels of theory.

State	Method <sup>a</sup>	$-E(547.)$	$R_e$	$D_e$	$\omega_e$	$\omega_e x_e$	$\alpha_e(10^{-4})$	$\bar{D}_e$ ( $10^{-7}$ )	$q_{\text{Ga}}$	$\langle \mu \rangle^b$	$\mu_{\text{FF}}^b$	$T_e$
$X^4\Sigma^-$	MRCI/CQZ-PP	0.810 065	2.4058	54.78	313.4	1.26	8.56	1.28	0.14	1.19	1.28	0.0
	MRCI+Q/CQZ-PP	0.853 74	2.406	56.0	312.9	1.27	8.56	1.28			1.33	0.0
	RCCSD(T)/CQZ-PP	0.873 917	2.4069	55.17	306.8	1.14	8.79	1.33			1.37	0.0
	MRCI/ACQZ-PP	0.810 582	2.4059	54.92	313.1	1.27	8.58	1.28	0.15	1.18	1.27	0.0
	MRCI+Q/ACQZ-PP	0.854 33	2.406	56.2	312.5	1.28	8.60	1.28			1.32	0.0
	RCCSD(T)/ACQZ-PP	0.874 589	2.4072	55.39	306.1	1.15	8.86	1.33			1.37	0.0
$a^2\Sigma^-$	MRCI/CQZ-PP	0.782 225	2.3914	37.31	320.8	1.35	8.81	1.26	0.14	1.49	1.44	17.47
	MRCI+Q/CQZ-PP	0.826 48	2.391	38.9	321.7	1.30	8.64	1.26			1.42	17.1
	MRCI/ACQZ-PP	0.782 876	2.3919	37.54	320.1	1.35	8.86	1.27	0.13	1.49	1.44	17.39
	MRCI+Q/ACQZ-PP	0.827 22	2.392	39.2	320.8	1.30	8.69	1.26			1.42	17.0
$1^2\Delta$	MRCI/CQZ-PP	0.777 774	2.4160	35.91	307.9	1.37	9.03	1.29	0.06	0.75	0.86	20.26
	MRCI+Q/CQZ-PP	0.824 21	2.414	37.9	307.6	1.36	9.06	1.30			0.93	18.5
	MRCI/ACQZ-PP	0.778 489	2.4165	36.18	307.4	1.38	9.06	1.29	0.07	0.751	0.87	20.14
	MRCI+Q/ACQZ-PP	0.825 07	2.415	38.2	306.8	1.37	9.10	1.30			0.94	18.4
$1^2\Pi_G$	MRCI/CQZ-PP	0.776 356	2.6054	34.09	252	11.3	1.82	1.22	0.11	0.69	0.72	21.15
	MRCI+Q/CQZ-PP	0.822 96	2.609	36.7	262	15.5	5.44	1.12			0.77	19.3
	RCCSD(T)/CQZ-PP	0.843 817	2.6223	36.28	254.6	0.94	6.76	1.15			0.77	18.89
	MRCI/ACQZ-PP	0.776 966	2.6043	34.67	246.9	5.09	0.36	1.28	0.11	0.68	0.71	21.09
	MRCI+Q/ACQZ-PP	0.823 74	2.608	37.2	258.1	4.44	4.27	1.16			0.76	19.2
	RCCSD(T)/ACQZ-PP	0.844 681	2.6240	36.62	253.2	0.93	6.83	1.16			0.78	18.77
$1^2\Pi_L$	MRCI/CQZ-PP	0.776 753	2.2515	34.34	358.9	2.75	12.47	1.45	0.04	1.41	1.43	20.90
	MRCI+Q/CQZ-PP	0.820 88	2.253	35.3	353.9	3.02	13.10	1.49			1.44	20.6
	RCCSD(T)/CQZ-PP	0.841 316	2.2536	34.72	356.1	2.19	11.90	1.46			1.43	20.46
	MRCI/ACQZ-PP	0.777 464	2.2516	34.98	358.9	2.72	12.34	1.45	0.03	1.42	1.44	20.78
	MRCI+Q/ACQZ-PP	0.821 71	2.253	36.0	353.8	3.01	12.95	1.49			1.45	20.5
	RCCSD(T)/ACQZ-PP	0.842 278	2.2540	35.11	355.7	2.18	11.92	1.47			1.45	20.28
$2^2\Pi$	MRCI/CQZ-PP	0.763 282	2.4317	27.86	495.7	13.02	5.10	0.479	0.07	0.37	0.80	29.36
	MRCI+Q/CQZ-PP	0.809 20	2.423	28.8	505.3	14.04	5.83	0.471			0.82	28.0
	MRCI/ACQZ-PP	0.763 913	2.4313	28.08	498.8	16.23	7.24	0.475	0.06	0.37	0.80	29.29
	MRCI+Q/ACQZ-PP	0.809 91	2.423	29.0	498.5	11.81	6.87	0.485			0.83	27.9
$1^2\Sigma^+$	MRCI/CQZ-PP	0.763 615	2.4351	27.02	297.5	1.50	9.42	1.32	0.05	0.61	0.58	29.15
	MRCI+Q/CQZ-PP	0.808 827	2.434	28.2	296.6	1.50	9.51	1.33			0.61	28.2
$1^4\Delta$	MRCI/CQZ-PP	0.724 549	3.1490	2.51	71.1	1.96	26.76	4.93	-0.08	1.44	1.43	53.66
	MRCI+Q/CQZ-PP	0.769 38	3.081	3.5	86.5	1.97	22.40	3.81			1.50	52.9
$1^4\Sigma^+$	MRCI/CQZ-PP	0.722 858	3.3040	1.45	51.8	1.38	29.1	6.99	-0.07	1.27	1.27	54.72
	MRCI+Q/CQZ-PP	0.767 54	3.183	2.3	70.2	1.72	24.1	4.74			1.42	54.1
$1^4\Pi$	MRCI(+Q)/CQZ-PP	Repulsive										
$2^4\Sigma^-$	MRCI(+Q)/CQZ-PP	Repulsive										
$2^4\Pi$	MRCI(+Q)/CQZ-PP	Repulsive										
$2^4\Pi$	MRCI/CQZ-PP	0.676 196	2.2524	-26.8 <sup>c</sup>	499.6	3.88	7.37	0.746	0.00	0.66	0.81	84.00
	MRCI+(Q)/CQZ-PP	0.721 37	2.238	-26.3 <sup>c</sup>	519.9	4.13	6.95	0.716			0.83	83.1
$1^6\Pi$	MRCI/CQZ-PP	0.648 531	2.3692	36.17 <sup>c</sup>	347.0	1.40	8.13	1.14	0.02	0.09	0.05	101.4
	MRCI+Q/CQZ-PP	0.687 73	2.365	39.8 <sup>c</sup>	348.3	1.38	8.08	1.14			0.03	104.2

<sup>a</sup>Internally contracted MRCI; +Q refers to the multireference Davidson correction.

<sup>b</sup> $\langle \mu \rangle$  refers to expectation values,  $\mu_{\text{FF}}$  to finite field values (field strength of  $10^{-4}$ ).

<sup>c</sup>The diabatic dissociation energy is 74.78 (79.4) for  $2^4\Pi$  and 57.14 (58.1) for  $1^6\Pi$  at the MRCI(+Q)/CQZ-PP level of theory.

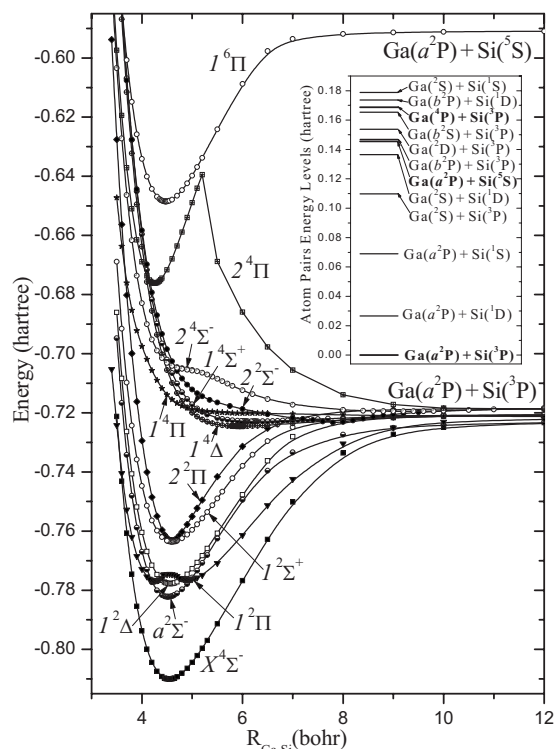


FIG. 1. MRCI/cc-pwCVQZ-PP<sub>Ga,cc-pVQZ<sub>Si</sub></sub> PECs of the GaSi molecules. All energies shifted by +547.0 hartrees. Inset: atomic limits of Ga+Si at MRCI+Q/aug-cc-pwCVQZ-PP<sub>Ga,aug-cc-pVQZ<sub>Si</sub></sub>.

The leading configuration and the Mulliken atomic distributions point clearly to two half  $\pi$  and one half  $\sigma$  bonds, as depicted in the following valence bond Lewis (vbl) diagram. About  $0.65 e^-$  is transferred from the  $4s^2 4p_z^1 (5s^2 5p_z^1)$  metal

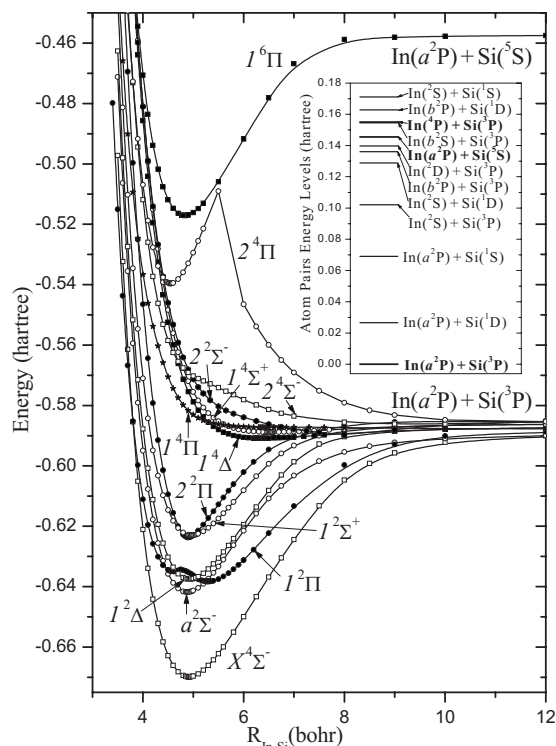


FIG. 2. MRCI/cc-pwCVQZ-PP<sub>In,cc-pVQZ<sub>Si</sub></sub> PECs of the InSi molecules. All energies shifted by +487.0 hartrees. Inset: atomic limits of In+Si at MRCI+Q/aug-cc-pwCVQZ-PP<sub>In,aug-cc-pVQZ<sub>Si</sub></sub>.

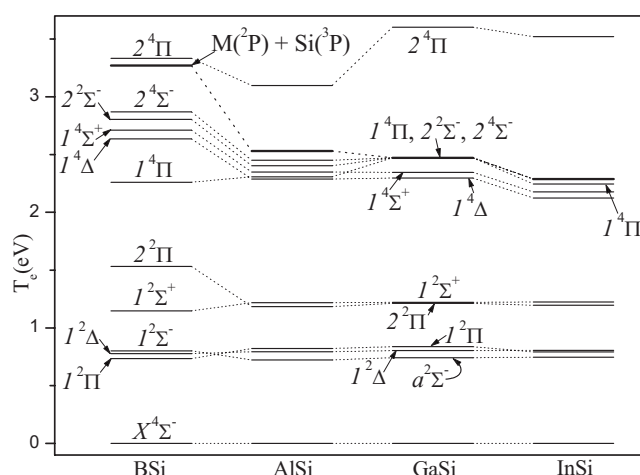
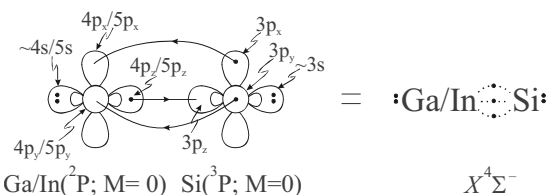


FIG. 3. MRCI+Q/cc-pwCVQZ-PP<sub>Ga,In,cc-pVQZ<sub>Si</sub></sub> relative energy levels of GaSi and InSi. The relative energy levels of BSi and AlSi have been taken by Ornellas and Iwata<sup>3,9</sup> at MRCI/cc-pVQZ level.

hybrid to the empty  $3p_z$  orbital of the Si atom, whereas  $\sim 0.5 e^-$  are transferred back to the Ga (In) atom through the  $\pi$  system.



The dissociation energies of the ground states of the GaSi and InSi molecules are  $D_e = 54.9(56.2)[55.4]$  and  $50.7(51.9)[51.5]$  kcal/mol at the MRCI(+Q)  $\times$  [RCCSD(T)]/ACQZ-PP level of theory (see Tables II and III). The bond lengths  $R_e$  are 2.406 and 2.603 Å at the MRCI+Q/ACQZ-PP level, respectively. The two molecules are similar to the  $X^4\Sigma^-$  state of InSi, having a  $D_e$  about 4 kcal/mol smaller and a  $R_e$  larger by 0.2 Å than the corresponding values of the  $X^4\Sigma^-$  state of GaSi. In the case of the isovalent BSi (Ref. 3) (AlSi) (Ref. 9) molecules, the  $D_e$  and  $R_e$  values of the  $X^4\Sigma^-$  state at the MRCI/cc-pVQZ level are  $D_e = 75.4(58.3)$  kcal/mol and  $R_e = 1.918(2.424)$  Å.

## B. $a^2\Sigma^-$

In both GaSi and InSi molecules, the  $a^2\Sigma^-$  state is the first excited state, it is well separated from the ground state  $X^4\Sigma^-$ , and it is located at about 17 kcal/mol higher (see Figs. 1 and 2). The only difference between  $X^4\Sigma^-$  and  $a^2\Sigma^-$  states is the spin. The open electrons are up-up-up in  $X^4\Sigma^-$  and up-down-up in  $a^2\Sigma^-$ . Thus, the  $a^2\Sigma^-$  states correlate with the ground state atoms Ga/In( $2P; M=0$ ) + Si( $3P; M=0$ ), maintaining this character throughout and the vbl diagram is as that of the ground states (see above). In both molecules, the bond length  $R_e$  of  $a^2\Sigma^-$  is 0.02 Å shorter than the  $R_e$  values of the  $X^4\Sigma^-$  state. The binding energy  $a^2\Sigma^-$  is  $D_e = 37.5(39.2)$  and  $33.2(34.8)$  for the two systems, respectively, at MRCI(+Q)/ACQZ-PP level of theory (see Tables II and III).

TABLE III. Absolute energies  $E$  (hartrees), bond lengths  $R_e$  (Å), binding energies  $D_e$  (kcal/mol), harmonic frequencies and anharmonic corrections  $\omega_e$ ,  $\omega_e x_e$  ( $\text{cm}^{-1}$ ), rotational vibrational couplings  $\alpha_e$  ( $\text{cm}^{-1}$ ), centrifugal distortions  $\bar{D}_e$  ( $\text{cm}^{-1}$ ), Mulliken charges on the indium  $q_{\text{In}}$ , dipole moments  $\mu$  (debye), and energy differences  $T_e$  (kcal/mol), of the indium silicide, InSi, at MRCI, MRCI+Q, and RCCSD(T)/cc-pwCVQZ-PP<sub>In,cc-pVQZ<sub>Si</sub></sub> (CQZ-PP) and aug-cc-pwCVQZ-PP<sub>In,aug-cc-pVQZ<sub>Si</sub></sub> (ACQZ-PP) levels of theory.

State	Method <sup>a</sup>	$-E(547.)$	$R_e$	$D_e$	$\omega_e$	$\omega_e x_e$	$\alpha_e$ ( $10^{-4}$ )	$\bar{D}_e$ ( $10^{-8}$ )	$q_{\text{In}}$	$\langle \mu \rangle^b$	$\mu_{\text{FF}}^b$	$T_e$
$X^4\Sigma^-$	MRCI/CQZ-PP	0.669 858	2.6000	50.55	272.1	0.95	5.38	7.36	0.16	1.76	1.94	0.0
	MRCI+Q/CQZ-PP	0.721 30	2.603	51.7	269.9	0.89	5.29	7.43			2.05	0.0
	RCCSD(T)/CQZ-PP	0.742 723	2.6016	51.24	265.0	0.81	5.76	7.73			2.11	0.0
	MRCI/ACQZ-PP	0.670 481	2.5997	50.72	272.0	0.98	5.38	7.37	0.22	1.75	1.94	0.0
	MRCI+Q/ACQZ-PP	0.722 01	2.603	51.9	269.7	0.91	5.27	7.44			2.05	0.0
	RCCSD(T)/ACQZ-PP	0.743 540	2.6018	51.51	264.7	0.92	5.92	7.74			2.12	0.0
$a^2\Sigma^-$	MRCI/CQZ-PP	0.641 780	2.5816	32.92	275.5	1.05	6.21	7.49	0.16	2.00	2.02	17.62
	MRCI+Q/CQZ-PP	0.693 86	2.583	34.5	275.0	0.98	6.09	7.49			2.04	17.2
	MRCI/ACQZ-PP	0.642 574	2.5819	33.22	275.1	1.05	6.24	7.51	0.18	2.00	2.03	17.51
	MRCI+Q/ACQZ-PP	0.694 78	2.584	34.8	274.4	0.97	6.11	7.51			2.05	17.1
$1^2\Delta$	MRCI/CQZ-PP	0.637 508	2.6059	31.62	266.0	1.11	6.25	7.60	0.07	1.13	1.35	20.30
	MRCI+Q/CQZ-PP	0.691 70	2.605	33.6	265.6	1.09	6.23	7.64			1.47	18.6
	MRCI/ACQZ-PP	0.638 339	2.6061	31.94	265.6	1.11	6.27	7.62	0.11	1.14	1.36	20.17
	MRCI+Q/ACQZ-PP	0.692 71	2.605	34.0	265.0	1.09	6.26	7.66			1.49	18.4
$1^2\Pi_G$	MRCI/CQZ-PP	0.638 250	2.8020	31.17	222	2.7	3.9	7.1	0.14	0.96	1.10	19.83
	MRCI+Q/CQZ-PP	0.692 21	2.794	33.4	229	2.4	5.4	6.7			1.17	18.3
	RCCSD(T)/CQZ-PP	0.714 695	2.8106	33.65	225.1	0.7	4.7	6.7			1.21	17.59
	MRCI/ACQZ-PP	0.639 007	2.8036	31.44	220	2.5	3.7	7.2	0.14	0.96	1.10	19.75
	MRCI+Q/ACQZ-PP	0.693 07	2.796	33.7	227	2.12	5.2	6.8			1.17	18.2
	RCCSD(T)/ACQZ-PP	0.715 701	2.8127	34.04	224	0.8	4.8	6.8			1.23	17.47
$1^2\Pi_L$	MRCI/CQZ-PP	0.634 948	2.4398	29.10	300	3.0	9.6	8.9	0.08	1.97	2.03	21.91
	MRCI+Q/CQZ-PP	0.686 96	2.443	30.1	293	3.7	10.5	9.2			2.07	21.5
	RCCSD(T)/CQZ-PP	0.708 679	2.4395	29.87	302	1.8	8.3	8.7			2.10	21.36
	MRCI/ACQZ-PP	0.635 765	2.4394	29.41	300	3.0	9.6	8.9	0.09	1.98	2.05	21.78
	MRCI+Q/ACQZ-PP	0.687 93	2.443	30.5	293	3.6	10.5	9.2			2.09	21.4
	RCCSD(T)/ACQZ-PP	0.709 803	2.4396	30.33	302	1.7	8.4	8.8			2.12	21.17
$2^2\Pi$	MRCI/CQZ-PP	0.623 655	2.5955	23.92	430.5	14.76	7.48	2.98	0.07	0.75	1.39	28.99
	MRCI+Q/CQZ-PP	0.677 33	2.586	24.9	441.8	16.06	7.32	2.90			1.47	27.6
	MRCI/ACQZ-PP	0.624 401	2.5954	24.18	427.7	14.71	8.11	3.02	0.09	0.75	1.40	28.92
	MRCI+Q/ACQZ-PP	0.678 19	2.586	25.2	436.4	15.12	8.01	2.96			1.48	27.5
$1^2\Sigma^+$	MRCI/CQZ-PP	0.622 948	2.6282	23.14	254.2	1.27	6.73	7.90	0.03	0.70	0.91	29.44
	MRCI+Q/CQZ-PP	0.676 31	2.625	24.2	254.4	1.26	6.73	7.95			1.01	28.2
$1^4\Delta$	MRCI/CQZ-PP <sup>c</sup>	0.590 880	3.3774	2.36	62.2	1.36	17.18	29.35	-0.07	1.42	1.37	49.56
	MRCI+Q/CQZ-PP <sup>c</sup>	0.643 22	3.311	3.2	73.9	1.33	14.41	23.37			1.42	49.0
$1^4\Sigma^+$	MRCI/CQZ-PP	0.588 845	3.4779	1.74	53.5	1.03	16.21	33.23	-0.06	1.30	1.28	50.84
	MRCI+Q/CQZ-PP	0.641 29	3.404	2.3	62.5	1.20	15.27	27.69			1.35	50.2
$1^4\Pi$	MRCI+Q/CQZ-PP	0.638 75	3.374	0.2							0.23	51.80
	MRCI+Q/ACQZ-PP	0.639 37	3.370	0.4							0.18	51.9
$2^2\Sigma^-$	MRCI(+Q)/CQZ-PP	Repulsive										
$2^2\Sigma^-$	MRCI(+Q)/CQZ-PP	Repulsive										
$2^4\Pi$	MRCI/CQZ-PP	0.539 588	2.4096	-28.8 <sup>d</sup>	417.5	2.63	6.32	4.93	0.03	1.04	1.36	81.75
	MRCI+Q/CQZ-PP	0.591 95	2.392	-28.7 <sup>d</sup>	434.7	2.86	6.25	4.75			1.42	81.2
$1^6\Pi$	MRCI/CQZ-PP	0.517 094	2.5567	37.47 <sup>d</sup>	298.9	1.14	5.69	6.74	0.04	0.42	0.52	95.86
	MRCI+Q/CQZ-PP	0.563 79	2.554	41.1 <sup>d</sup>	299.5	1.14	5.67	6.76			0.57	98.8

<sup>a</sup>Internally contracted MRCI; +Q refers to the multireference Davidson correction.

<sup>b</sup> $\langle \mu \rangle$  refers to expectation values,  $\mu_{\text{FF}}$  to finite field values (field strength of  $10^{-4}$ ).

<sup>c</sup> $R_e=3.3683$  (3.303) and  $D_e=2.51$  (3.36) at MRCI(+Q)/ACQZ-PP level of theory.

<sup>d</sup>The diabatic dissociation energy is 63.61 (68.1) for  $2^4\Pi$  and 49.50 (50.5) for  $1^6\Pi$  at the MRCI(+Q)/CQZ-PP level of theory.

TABLE IV. MRCI/cc-pwCVQZ-PP<sub>Ga,In</sub> cc-pVQZ-Si atomic Mulliken populations of the calculated binding states of the GaSi(InSi) molecules.

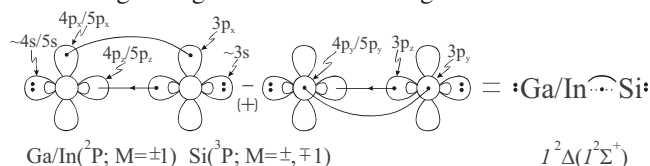
State <sup>a</sup>	Ga(In)				Si				Equilibrium leading configuration
	4(5)s	4(5)p <sub>z</sub>	4(5)p <sub>x</sub>	4(5)p <sub>y</sub>	3s	3p <sub>z</sub>	3p <sub>x</sub>	3p <sub>y</sub>	
X <sup>4</sup> Σ <sup>-</sup>	1.77(1.79)	0.54(0.55)	0.23(0.21)	0.23(0.21)	1.79(1.79)	0.77(0.74)	0.75(0.78)	0.75(0.78)	0.92(0.93) 1σ <sup>2</sup> 2σ <sup>2</sup> 3σ <sup>2</sup> 4σ <sup>1</sup> 1π <sub>x</sub> <sup>2</sup> 2π <sub>x</sub> <sup>1</sup> 1π <sub>y</sub> <sup>2</sup> 2π <sub>y</sub> <sup>1</sup> 1δ <sub>x</sub> <sup>1</sup> 1δ <sub>z</sub> <sup>2</sup>
a <sup>2</sup> Σ <sup>-</sup>	1.74(1.75)	0.58(0.59)	0.23(0.21)	0.23(0.21)	1.78(1.78)	0.77(0.75)	0.74(0.77)	0.74(0.77)	0.80(0.79) 1σ <sup>2</sup> 2σ <sup>2</sup> 3σ <sup>2</sup> 4σ <sup>1</sup> 1π <sub>x</sub> <sup>2</sup> 2π <sub>x</sub> <sup>1</sup> 1π <sub>y</sub> <sup>2</sup> 2π <sub>y</sub> <sup>1</sup> 1δ <sub>x</sub> <sup>1</sup> 1δ <sub>z</sub> <sup>2</sup> +0.46(0.46) 1σ <sup>2</sup> 2σ <sup>2</sup> 3σ <sup>2</sup> 4σ <sup>1</sup> 1π <sub>x</sub> <sup>2</sup> 2π <sub>x</sub> <sup>1</sup> 1π <sub>y</sub> <sup>2</sup> 2π <sub>y</sub> <sup>1</sup> 1δ <sub>x</sub> <sup>1</sup> 1δ <sub>z</sub> <sup>2</sup>
1 <sup>2</sup> Δ	1.74(1.75)	0.51(0.52)	0.31(0.29)	0.31(0.29)	1.82(1.82)	0.80(0.79)	0.68(0.69)	0.68(0.69)	0.65(0.64) 1σ <sup>2</sup> 2σ <sup>2</sup> 3σ <sup>2</sup> 4σ <sup>1</sup> (1π <sub>x</sub> <sup>2</sup> 2π <sub>x</sub> <sup>1</sup> 1π <sub>y</sub> <sup>2</sup> -1π <sub>x</sub> <sup>1</sup> 1π <sub>y</sub> <sup>2</sup> 2π <sub>y</sub> <sup>1</sup> 1δ <sub>x</sub> <sup>1</sup> 1δ <sub>z</sub> <sup>2</sup> )
1 <sup>2</sup> Π <sub>G</sub>	1.84(1.84)	0.74(0.76)	0.15(0.13)	0.07(0.07)	1.86(1.86)	1.29(1.28)	0.85(0.88)	0.07(0.08)	0.91(0.90) 1σ <sup>2</sup> 2σ <sup>2</sup> 3σ <sup>2</sup> 4σ <sup>1</sup> 1π <sub>x</sub> <sup>2</sup> 2π <sub>x</sub> <sup>1</sup> 1π <sub>y</sub> <sup>2</sup> 1δ <sub>x</sub> <sup>1</sup> 1δ <sub>z</sub> <sup>2</sup>
1 <sup>2</sup> Π <sub>L</sub>	1.62(1.62)	0.24(0.24)	0.30(0.27)	0.73(0.72)	1.70(1.72)	0.35(0.35)	0.70(0.73)	1.20(1.21)	0.89(0.88) 1σ <sup>2</sup> 2σ <sup>2</sup> 3σ <sup>2</sup> 1π <sub>x</sub> <sup>2</sup> 2π <sub>x</sub> <sup>1</sup> 1π <sub>y</sub> <sup>2</sup> 2π <sub>y</sub> <sup>1</sup> 1δ <sub>x</sub> <sup>1</sup> 1δ <sub>z</sub> <sup>2</sup>
2 <sup>2</sup> Π	1.80(1.78)	0.63(0.62)	0.21(0.19)	0.23(0.27)	1.81(1.81)	1.02(0.96)	0.79(0.81)	0.36(0.42)	0.78(0.74) 1σ <sup>2</sup> 2σ <sup>2</sup> 3σ <sup>2</sup> 4σ <sup>1</sup> 1π <sub>x</sub> <sup>2</sup> 2π <sub>x</sub> <sup>1</sup> 1π <sub>y</sub> <sup>2</sup> 1δ <sub>x</sub> <sup>1</sup> 1δ <sub>z</sub> <sup>2</sup> +0.45(0.48) 1σ <sup>2</sup> 2σ <sup>2</sup> 3σ <sup>2</sup> 1π <sub>x</sub> <sup>2</sup> 2π <sub>x</sub> <sup>1</sup> 1π <sub>y</sub> <sup>2</sup> 2π <sub>y</sub> <sup>1</sup> 1δ <sub>x</sub> <sup>1</sup> 1δ <sub>z</sub> <sup>2</sup>
1 <sup>2</sup> Σ <sup>+</sup>	1.74(1.74)	0.50(0.48)	0.33(0.34)	0.33(0.34)	1.81(1.81)	0.82(0.82)	0.67(0.67)	0.67(0.67)	0.64(0.63) 1σ <sup>2</sup> 2σ <sup>2</sup> 3σ <sup>2</sup> 4σ <sup>1</sup> (1π <sub>x</sub> <sup>2</sup> 2π <sub>x</sub> <sup>1</sup> 1π <sub>y</sub> <sup>2</sup> +1π <sub>x</sub> <sup>1</sup> 1π <sub>y</sub> <sup>2</sup> 2π <sub>y</sub> <sup>1</sup> 1δ <sub>x</sub> <sup>1</sup> 1δ <sub>z</sub> <sup>2</sup> )
1 <sup>4</sup> Δ	1.88(1.88)	0.16(0.14)	0.51(0.51)	0.51(0.51)	1.92(1.93)	0.93(0.95)	0.51(0.51)	0.51(0.51)	0.66(0.66) 1σ <sup>2</sup> 2σ <sup>2</sup> 3σ <sup>2</sup> 4σ <sup>1</sup> (1π <sub>x</sub> <sup>2</sup> 2π <sub>x</sub> <sup>1</sup> 3π <sub>x</sub> <sup>1</sup> 1π <sub>y</sub> <sup>2</sup> -1π <sub>x</sub> <sup>1</sup> 1π <sub>y</sub> <sup>2</sup> 2π <sub>y</sub> <sup>1</sup> 3π <sub>y</sub> <sup>1</sup> )1δ <sub>x</sub> <sup>1</sup> 1δ <sub>z</sub> <sup>2</sup>
1 <sup>4</sup> Σ <sup>+</sup>	1.90(1.89)	0.13(0.12)	0.51(0.51)	0.51(0.51)	1.93(1.93)	0.95(0.95)	0.51(0.51)	0.51(0.51)	0.66(0.65) 1σ <sup>2</sup> 2σ <sup>2</sup> 3σ <sup>2</sup> 4σ <sup>1</sup> (1π <sub>x</sub> <sup>2</sup> 2π <sub>x</sub> <sup>1</sup> 3π <sub>x</sub> <sup>1</sup> 1π <sub>y</sub> <sup>2</sup> +1π <sub>x</sub> <sup>1</sup> 1π <sub>y</sub> <sup>2</sup> 2π <sub>y</sub> <sup>1</sup> 3π <sub>y</sub> <sup>1</sup> )1δ <sub>x</sub> <sup>1</sup> 1δ <sub>z</sub> <sup>2</sup>
2 <sup>4</sup> Π	1.41(1.35)	0.40(0.44)	0.30(0.27)	0.83(0.84)	1.59(1.61)	0.53(0.54)	0.70(0.71)	1.10(1.10)	0.68(0.71) 1σ <sup>2</sup> 2σ <sup>2</sup> 3σ <sup>1</sup> 4σ <sup>1</sup> 1π <sub>x</sub> <sup>2</sup> 2π <sub>x</sub> <sup>1</sup> 1π <sub>y</sub> <sup>2</sup> 2π <sub>y</sub> <sup>1</sup> 1δ <sub>x</sub> <sup>1</sup> 1δ <sub>z</sub> <sup>2</sup> -0.60(0.54) 1σ <sup>2</sup> 2σ <sup>2</sup> 3σ <sup>2</sup> 1π <sub>x</sub> <sup>2</sup> 2π <sub>x</sub> <sup>1</sup> 1π <sub>y</sub> <sup>2</sup> 2π <sub>y</sub> <sup>1</sup> 3π <sub>y</sub> <sup>1</sup> 1δ <sub>x</sub> <sup>1</sup> 1δ <sub>z</sub> <sup>2</sup>
1 <sup>6</sup> Π	1.22(1.17)	0.54(0.56)	0.19(0.17)	0.97(0.98)	1.46(1.50)	0.72(0.69)	0.80(0.81)	0.97(0.97)	0.95(0.95) 1σ <sup>2</sup> 2σ <sup>2</sup> 3σ <sup>1</sup> 4σ <sup>1</sup> 1π <sub>x</sub> <sup>2</sup> 2π <sub>x</sub> <sup>1</sup> 1π <sub>y</sub> <sup>2</sup> 2π <sub>y</sub> <sup>1</sup> 3π <sub>y</sub> <sup>1</sup> 1δ <sub>x</sub> <sup>1</sup> 1δ <sub>z</sub> <sup>2</sup>

<sup>a</sup>G refers to the global minimum and L refers to the local minimum.

In the case of the BSi<sup>3</sup> molecule, the <sup>2</sup>Σ<sup>-</sup> state is reported as the third excited state lying at 18.5 kcal/mol above the X<sup>4</sup>Σ<sup>-</sup> state, at MRCI/cc-pVQZ. However, in AlSi at the same level,<sup>9</sup> the <sup>2</sup>Σ<sup>-</sup> state is the first excited state, as in the present calculations on the GaSi and InSi molecules, lying 16.7 kcal/mol above the ground state.

### C. 1<sup>2</sup>Δ and 1<sup>2</sup>Σ<sup>+</sup>

The 1<sup>2</sup>Δ and 1<sup>2</sup>Σ<sup>+</sup> states of GaSi and InSi correlate with Ga/In(<sup>2</sup>P;M=±1)+Si(<sup>3</sup>P;M=±1 and ∓1), respectively, maintaining this character throughout. A full π and a half σ bond are observed. About 0.4 e<sup>-</sup> transfer through the π-system from the metal atom to Si and 0.3 e<sup>-</sup> transfer from the 3p<sub>z</sub> atomic orbital of Si to the empty p<sub>z</sub> (M=0) orbital of Ga(In) as can be seen by the Mulliken atomic distributions (Table IV) and as depicted in the following vbL diagram. The 1<sup>2</sup>Δ and 1<sup>2</sup>Σ<sup>+</sup> states differ in the sign “-” and “+” in the leading configuration and vbL diagrams.



In both molecules, the 1<sup>2</sup>Δ and 1<sup>2</sup>Σ<sup>+</sup> states are found at about 18.5 and 28.2 kcal/mol above the ground states X<sup>4</sup>Σ<sup>-</sup> (see Figs. 1 and 2 and Tables II and III). At the highest level

of theory MRCI(+Q)/ACQZ-PP, the binding energies of the 1<sup>2</sup>Δ states are D<sub>e</sub>=36.2 (38.2) and 31.9 (34.0) kcal/mol for the GaSi and InSi, respectively. The corresponding bond lengths R<sub>e</sub> are 2.415 and 2.605 Å at the MRCI+Q/ACQZ-PP level, respectively. For the 1<sup>2</sup>Σ<sup>+</sup> states, the dissociation energies are about 10 kcal/mol smaller and the bond lengths are 0.02 Å shorter than the corresponding values of the 1<sup>2</sup>Δ states in both molecules (see Tables II and III).

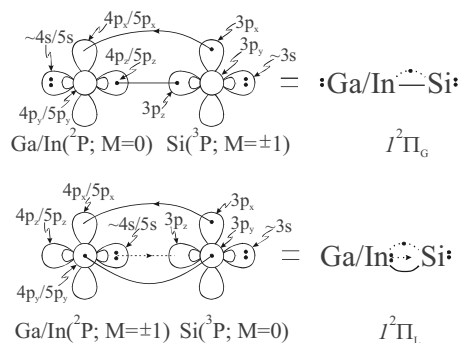
### D. 1<sup>2</sup>Π and 2<sup>2</sup>Π

The 1<sup>2</sup>Π state is found at 19.2 kcal/mol (GaSi) and 18.2 kcal/mol (InSi) above the X<sup>4</sup>Σ<sup>-</sup> one and it presents two minima, one of which results from an avoided crossing with 2<sup>2</sup>Π (see Figs. 1 and 2) with similar D<sub>e</sub> at MRCI and RCCSD(T) in both basis sets (see Figs. 1 and 2). However, in the case of the InSi molecule at the MRCI+Q level (i.e., where the quadruple-CI correction is included), the second minimum is found to be a shoulder rather than a clear second minimum. The barrier between the global and the local minima 1<sup>2</sup>Π<sub>G</sub>→1<sup>2</sup>Π<sub>L</sub> is 1.1 (1.5) kcal/mol for GaSi and 2.3 kcal/mol for InSi at MRCI(+Q) with both CQZ-PP and ACQZ-PP basis sets.

The 1<sup>2</sup>Π state correlates with Ga/In(<sup>2</sup>P;M=0)+Si(<sup>3</sup>P;M=±1) and maintains this character up to the first minimum. This is typically the global minimum at 2.608[2.624] Å with a D<sub>e</sub>=37.5[36.6] for GaSi and at 2.796[2.813] Å with a D<sub>e</sub>=33.7[34.0] for InSi at the MRCI+Q [RCCSD(T)]/ACQZ-PP level of theory. Then,

around 4.6 bohrs (GaSi) and 4.9 bohrs (InSi), the  $1^2\Pi$  state interacts with the  $2^2\Pi$ , thus it changes its character to Ga/In ( $^2P; M = \pm 1$ ) + Si ( $^3P; M = 0$ ) (Figs. 1 and 2). The local minimum is located at 2.253[2.254] Å with a  $D_e = 36.0$ [35.1] for GaSi and at 2.443[2.440] Å with a  $D_e = 30.5$ [30.3] for InSi at the MRCI+Q[RCCSD(T)]/ACQZ-PP level of theory.

At the global minimum, a whole  $\sigma$  bond and a half  $\pi$  bond are observed for the  $1^2\Pi$  state in both GaSi and InSi. About  $0.3 e^-$  transfer from the  $p_z$  atomic orbital of Ga/In to the  $3p_z$  orbital of Si and  $0.15 e^-$  are backdonated from the  $3p_x$  atomic orbital of Si to the empty  $p_x$  of Ga/In (see Table IV). At the local minimum, a whole  $\pi$  and a half  $\pi$  bond are observed and a small transfer from the  $4s/5s$  atomic orbital of metal to the empty  $p_z$  atomic orbital of Si. The vBL diagrams of the two minima are as follows.

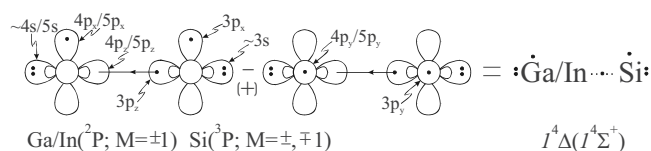


The  $2^2\Pi$  state presents a minimum at 2.423 Å (GaSi) and 2.586 Å (InSi), i.e., at the avoided crossing of the two adiabatic curves of  $2^2\Pi$  symmetry. The binding energies are 29.0 kcal/mol (GaSi) and 25.2 kcal/mol (InSi) at the MRCI+Q/ACQZ-PP level of theory.

In the BSi (Ref. 3) and AlSi (Ref. 9) molecules avoided crossing between the adiabatic PECs of the  $1^2\Pi$  and  $2^2\Pi$  states are also found. However, in the case of the BSi, the  $1^2\Pi$  state (reported as the first excited state lying at 16.9 kcal/mol above the ground state<sup>3</sup>) presents only one minimum,<sup>3</sup> which corresponds to the second (local) minimum of the GaSi and InSi molecules, and a shoulder at larger R. In the case of AlSi (Ref. 9) the  $1^2\Pi$  state has a very flat potential-well minimum, meaning that the two minima are jointed, while in the case of GaSi, as shown above, the two minima are separated and in the InSi case the two minima are separated in MRCI but in MRCI+Q the second minimum is rather a shoulder.

### E. $1^4\Delta$ and $1^4\Sigma^+$

These states have shallow van der Waals minima with a dissociation energies of about 3.5( $1^4\Delta$ ) and 2.3( $1^4\Sigma^+$ ) kcal/mol for both molecules (see Tables II and III). The  $1^4\Delta$  and  $1^4\Sigma^+$  states correlate with Ga/In ( $^2P; M = \pm 1$ ) + Si ( $^3P; M = \pm 1$  and  $\mp 1$ ) and maintain their character throughout. A weak half  $\sigma$  bond is observed and  $0.1 e^-$  transfers from the  $3p_z$  atomic orbital of Si to the empty  $p_z$  orbital of Ga(In) (see Table IV). Pictorially, the vBL diagram is as follows.

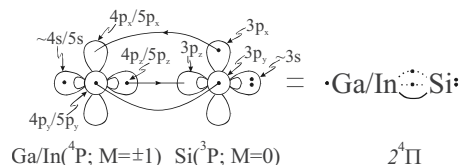


### F. $2^2\Sigma^-$ and $2^4\Sigma^-$

They are repulsive for both molecules and correlate with Ga/In ( $^2P; M = \pm 1$ ) + Si ( $^3P; M = \mp 1$ ). The  $2^2\Sigma^-$  states maintain their character in their whole potential energy curves, while the  $2^4\Sigma^-$  states present an avoided crossing at  $\sim 5$  bohrs with a  $3^4\Sigma^-$  state and the new character at shorter R is Ga/In ( $4^2P$ ) + Si ( $^3P$ ).

### G. $1^4\Pi$ and $2^4\Pi$

The  $1^4\Pi$  states also correlate with the atomic ground state limits, Ga/In ( $^2P; M = \pm 1$ ) + Si ( $^3P; M = 0$ ). Practically, they are repulsive. Only for InSi, the curve is very slightly bound, 0.38 kcal/mol at the MRCI+Q/ACQZ-PP level of theory. The  $2^4\Pi$  states correlate with Ga/In ( $^2P; M = 0$ ) + Si ( $^3P; M = \pm 1$ ) and they are unbound, with a local minimum as a result of an avoided crossing with higher  $4^2\Pi$  states at 5.2 bohrs (GaSi) and 5.5 bohrs (InSi) (see Figs. 1 and 2). Judging from the population analyses, the leading configurations along the curves, and calculation of some higher  $4^2\Pi$  states at CASSCF level of theory, we conclude that the  $2^4\Pi$  states at short R obtain a character Ga/In ( $4^2P; M = \pm 1$ ) + Si ( $^3P; M = 0$ ). It might be noted that the diabatic curves with the above character cross eight  $4^2\Pi$  states before the crossing with the  $2^4\Pi$  states, i.e., one  $4^2\Pi$  resulting from Ga/In ( $^2S$ ) + Si ( $^3P$ ), two  $4^2\Pi$  from Ga/In ( $b^2P$ ) + Si ( $^3P$ ), one  $4^2\Pi$  from Ga/In ( $a^2P$ ) + Si ( $^5S$ ), three  $4^2\Pi$  from Ga/In ( $^2D$ ) + Si ( $4P$ ), and one  $4^2\Pi$  from Ga/In ( $b^2S$ ) + Si ( $^3P$ ) (see insets in Figs. 1 and 2). As mentioned, the  $2^4\Pi$  states are unbound with respect to the atomic ground state products, with the local minima lying at 26.3 kcal/mol (GaSi) and 28.7 kcal/mol (InSi) above the respective atomic ground state products. However, with respect to diabatic products Ga/In ( $4^2P$ ) + Si ( $^3P$ ),  $D_e = 79.4$  kcal/mol (GaSi) and 68.1 kcal/mol (InSi) at the MRCI+Q/CQZ-PP level of theory. A half  $\sigma$ , a whole  $\pi$ , and a half  $\pi$  bond are formed. Pictorially, the bonding is as follows.

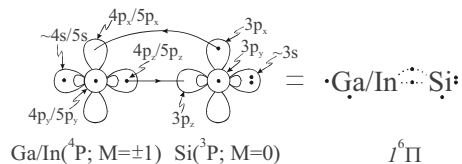


An additional avoided crossing is found at about 4.2 bohrs between the  $2^4\Pi$  and  $1^4\Pi$  states in both systems.

### H. $1^6\Pi$

This state is the lowest of the sextet states. It correlates with Ga/In ( $^2P; M = \pm 1$ ) + Si ( $^5S$ ) but for R near 7 bohrs it suffers an avoided crossing with the  $2^6\Pi$  state, therefore the *in situ* equilibrium character becomes Ga/In ( $4^2P; M = \pm 1$ ) + Si ( $^2P; M = 0$ ). Two half  $\sigma$  and  $\pi$  bonds are observed, the

result of about  $0.2 e^-$  transfer from the  $3p_x$  atomic orbital of Si to the empty  $p_x$  orbital of Ga/In, with a backtransfer of  $0.2 e^-$  from the  $p_z$  of Ga/In to  $3p_z$  atomic orbital of Si. Pictorially, the vbL diagram is as follows.



The binding energy of the  $1^6\Pi$  state, with respect to  $\text{Ga/In}(^2\text{P})+\text{Si}(^5\text{S})$ , is  $D_e=39.8$  kcal/mol (GaSi) and 41.1 kcal/mol (InSi), while the diabatic  $D_e$  with respect to  $\text{Ga/In}(^4\text{P})+\text{Si}(^2\text{P})$  is  $D_e=58.1$  kcal/mol (GaSi) and 50.5 kcal/mol (InSi) (see Tables II and III). The bond lengths are 2.365 Å (GaSi) and 2.554 Å (InSi) at the MRCI+Q/CQZ-PP level of theory.

The 12 states that result from the ground states of  $\text{Ga/In}(^2\text{P})$  and  $\text{Si}(^3\text{P})$  exhibit a spread at 12 bohrs in Figs. 1 and 2. However, the asymptotic spread is less than 4 mhartrees at the MRCI and 1 mhartrees at the MRCI+Q level of theory as calculated at 30 bohrs. Spin-orbit effects have not been taken into account in the present study. In the case of the InSi molecule spin-orbit effects could cause a small change in the shapes of the PECs. However, for both molecules GaSi and InSi, the ground states are  $\Sigma$  states and they are well separated from the excited states. Thus, it is unlikely for the calculated data of the ground state to change because of the spin-orbit coupling.

The relative energies of the molecular states of the isovalent MSi molecules,  $M=\text{B, Al, Ga, and In}$  are depicted in Fig. 3. The data for the BSi and AlSi molecules at MRCI/cc-pVQZ level of theory were taken by Ornellas and Iwata.<sup>3,9</sup> All four molecules have a  $X^4\Sigma^-$  as a ground state followed by three closely lying states  $1^2\Pi$ ,  $1^2\Delta$ , and  $1^2\Sigma^-$ . This ordering is found for BSi,<sup>3</sup> while for the next two molecules the ordering is reversed, i.e.,  $1^2\Sigma^-$ ,  $1^2\Delta$ , and  $1^2\Pi$  and for InSi the ordering is  $1^2\Sigma^-$ ,  $1^2\Pi$ , and  $1^2\Delta$ . The next excited states are the  $1^2\Sigma^+$  and  $2^2\Pi$ , which are well separated for BSi, but they are almost energetically degenerate and with a reverse ordering for the remaining three molecules. The next five states are also well separated in BSi and bound with respect to the atomic ground state products. In AlSi they are also bound but with less binding energy and they are more close lying to each other. For GaSi and InSi, some of these five states are found to be unbound (see Fig. 3).

Finally, the dipole transition moments for transitions involving the two lowest states  $X^4\Sigma^-$  and  $a^2\Sigma^-$  states were determined. In Table V, the absorption oscillator strength and the A Einstein coefficient for the emission of some dipole allowed transitions are given. The corresponding radiative lifetimes are  $4.3(4.2)\times 10^{-5}$  s for the  $2^2\Pi$  state,  $6.7(4.4)\times 10^{-4}$  s for  $1^2\Sigma^+$ , and  $8.2(3.3)\times 10^{-7}$  s for  $2^4\Pi$  of the GaSi (InSi) molecules at the MRCI/CQZ-PP level of theory. The radiative lifetimes have been estimated on the basis of the vertical electronic dipole transition moments to all possible lower states at the minimum of the excited states. The data are similar for the two molecules as expected because of the similarity of the corresponding PECs. The estimated os-

TABLE V. Oscillator strengths,  $F_L$  (at  $R_{\min}$  of the lowest state), for absorption and A Einstein coefficients,  $A_v$  ( $s^{-1}$ ) (at  $R_{\min}$  of the upper state), for emission of the dipole-allowed transitions of the GaSi and InSi molecules at MRCI/cc-pwCVQZ-PP<sub>Ga,In</sub> cc-pVQZ<sub>Si</sub> level of theory.

	GaSi		InSi	
	$F_L$	$A_v$	$F_L$	$A_v$
$X^4\Sigma^- - 1^4\Pi$	$1.49 \times 10^{-3}$		$2.00 \times 10^{-3}$	
$X^4\Sigma^- - 2^4\Pi$	$1.35 \times 10^{-3}$	$1.01 \times 10^6$	$4.43 \times 10^{-3}$	$2.59 \times 10^6$
$X^4\Sigma^- - 2^4\Sigma^-$	$1.38 \times 10^{-3}$		$5.78 \times 10^{-3}$	
$a^2\Sigma^- - 1^2\Pi$	$1.38 \times 10^{-4}$		$9.73 \times 10^{-5}$	
$a^2\Sigma^- - 2^2\Pi$	$2.40 \times 10^{-3}$	$1.65 \times 10^4$	$2.42 \times 10^{-3}$	$1.53 \times 10^4$
$a^2\Sigma^- - 2^2\Sigma^-$	$2.61 \times 10^{-4}$		$3.90 \times 10^{-4}$	

illator strengths suggest that the transitions in absorption are weak and their values follow the selection rules for Hund case a diatomics. The  $X^4\Sigma^- - 2^4\Pi$  transition is predicted to be stronger than  $a^2\Sigma^- - 2^2\Pi$  in emission.

#### IV. SUMMARY

Employing multireference variational (MRCI) and coupled cluster [RCCSD(T)] methods combined with quantitative basis sets, we have calculated 13 states of the GaSi and InSi molecules. The correlation consistent cc-pVQZ and aug-cc-pVQZ basis sets for Si were used in combination with the correlation consistentlike weighted core basis sets, i.e., cc-pwCVQZ-PP and aug-cc-pwCVQZ-PP for Ga and In. These employ an accurate small-core relativistic pseudopotentials and they are developed specifically for the 3d (4d) correlation, which we need to include in our calculation in order to obtain accurate results.

For all states we report on full PECs, energetics, and spectroscopic parameters, dipole moments calculated as expectation values ( $\langle \mu \rangle$ ), and also by the finite field method ( $\mu_{\text{FF}}$ ). A summary of our main results follows.

- For both molecules, the ground state is of  $4\Sigma^-$  symmetry, with a  $D_e$  ( $D_0$ ) value of 56.2 (55.7) kcal/mol at  $r_e=2.406$  Å for GaSi and 51.9 (51.5) kcal/mol at  $r_e=2.603$  Å for InSi.
- The first excited state is the  $2\Sigma^-$  state, lying 17 kcal/mol above the ground state, with  $D_e=39.2$  kcal/mol (GaSi) and 34.8 kcal/mol (InSi). In both molecules, the bond length,  $R_e$ , is 0.02 Å shorter than the  $R_e$  values of the  $X^4\Sigma^-$  state.
- Six out of the 12 states, which result from the ground states of  $\text{Ga/In}(^2\text{P})$  and  $\text{Si}(^3\text{P})$ , are bound with  $D_e$  ranging from 56.2 to 28.2 kcal/mol (GaSi) and 51.9 to 24.2 kcal/mol (InSi). For both molecules, two states are van der Waals states with a  $D_e$  ranging from 2.3 to 3.5 kcal/mol, three states are practically unbound and the last one is unbound with respect to asymptotic products but bound with respect to diabatic products by 79.4 kcal/mol (GaSi) and 68.1 kcal/mol (InSi). This last state has the shortest bond length of all calculated states 2.238 Å (GaSi) and 2.392 Å (InSi).



- (iv) Small charge transfer is found from metal to Si ranging from 0.2 to  $-0.1 e^-$ .
- (v) For the calculated states, practically there are no differences between augmented and nonaugmented basis sets.
- (vi) The GaSi and InSi molecules are very similar molecules. Their electronic states have practically the same ordering (with the exception of  $1^2\Delta$  and  $1^2\Pi$ ), the same bonding and present the same avoided crossings. Their PECs have similar shapes. For all calculated states, the bond lengths of InSi are larger by about  $0.2 \text{ \AA}$  and their dissociation energies are smaller than the corresponding values of GaSi. Specifically, for the six lowest bound states of InSi, their  $D_e$  values are smaller by 3–4 kcal/mol than the corresponding  $D_e$  values of the GaSi molecule.
- (vii) Finally, the GaSi and InSi molecules present similarities with the isovalent BSi and AlSi molecules and mainly with the last one.

The present study provides fundamental information regarding the electronic structure of the diatomic molecules GaSi and InSi given the complete lack of relevant theoretical or experimental information. Such information can be of use to researchers studying gas phase and surface reactions and spectra involving these molecules. It can also be used as a base for the selection of an appropriate method of calculation on surfaces containing Ga, In, and Si and the epitaxy of group IIIA films on the Si surfaces.

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