Theoretical Studies of the Low-Lying States of $GeSi^+$

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Electronic structure and spectroscopic properties of the ground and low-lying excited states of $GeSi^+$ have been studied by using multireference singles and doubles configuration interaction (MRDCI) method that includes relativistic effective core potentials of Ge and Si atoms. At least 17 $\Lambda-\Sigma$ bound states of $GeSi^+$ are reported within 5 eV. Potential energy curves of 24 $\Lambda-\Sigma$ states which correlate with the lowest two dissociation limits, $Ge^+(^2P_u)+Si(^3P_g)$ and $Ge(^3P_g)+Si^+(^2P_u)$ are constructed. The ground-state dissociation energy of $GeSi^+$ is estimated to be 3.116 eV. The spin−orbit coupling among all states correlating the two dissociation limits is also included in the calculations. Spectroscopic constants of 27 Ω states of the ion are reported. Effects of the spin−orbit coupling on the spectroscopic properties are also studied. Potential energy curves of Ω states show several avoided crossings. Transition probabilities of many electric dipole allowed and spin-forbidden transitions are computed. Transitions such as $2^4\Sigma^- - X^4\Sigma^-$ and $4^4\Sigma^- - X^4\Sigma^-$ are found to be highly probable. Partial lifetimes for some weak spin-forbidden transitions to the ground-state components, $X^4\Sigma^-_{1/2}$ and $X^4\Sigma^-_{3/2}$ are also computed.

I. Introduction

Molecules of group IV atoms have technological importance because of their large scale applications in the optoelectronics and semiconductor industries.[1−6] The chemical vapor deposition technique is used to form semiconductor films with these materials. The binary heterostructure $Si/Si_{1-x}Ge_x$ has produced a new generation high performance heterojunction bipolar transistors, field effect transistors and infrared photodetectors,[3,4] solar cells,[5] etc. The element germanium, which possesses very high electron and hole mobilities, makes it a viable alternative for high speed microelectronic chips. It is essential to study the nature of the chemical bonding to understand the chemical and physical properties of these semiconductor materials so that the quality of these materials can be improved.

Although a large volume of data is available on the solid state materials of Ge/Si, experimental and theoretical studies of small clusters or small molecules and ions are not so large. Diatomic molecules like GeC and GeSi are seldom studied, possibly because of the experimental difficulties in preparing their gas phase samples. Dissociation energies of GeC and GeSi molecules using Knudsen effusion mass spectrometric technique have been reported.[7,8] DFT calculations were performed recently by Li et al.[9] to study the structural and electronic properties of binary microclusters A_mB_n (A, B = Si, Ge, C). The infrared spectra of GeSi and SnSi in argon matrices at 4K were recorded[10] for frequencies up to 3000 cm^{-1}. The vibrational progression for the $X'^3\Pi \leftarrow X^3\Sigma^-$ transition was also observed.

Potential energy curves (PECs) for the ground and a few low-lying states namely, $^3\Pi$, $^1\Sigma^+$, and $^1\Delta$ of GeSi were first constructed by Andzelm et al.[11] from the local spin-density calculations. Later on, ab initio calculations at the multireference CI level were carried out by Sefyani et al.[12] for determining energies and structural properties of the valence electronic states of GeSi below 30 000 cm^{-1}. In a related calculation, these authors reported[13] spectroscopic properties of six lowest states of $GeSi^+$, supplementing their earlier results of the neutral species. Sari et al.[14] studied $^3\Sigma^-$ and $^3\Pi$ states of GeC and GeSi using the highly correlated coupled-cluster theory. Ueno et al.[15] theoretically investigated the photoelectron spectra of GeC, GeSi, and their monopositive ions using MRCI calculations with an extensive basis set like aug-cc-pVQZ. The Franck−Condon (FC) factors and ionization energies for both $GeC \rightarrow GeC^+$ and $GeSi \rightarrow GeSi^+$ were computed. Recently, a number of Ge_nSi_m ($m + n = 5$) clusters were studied by Wielgus et al.[16] at MP2, MP2//CCSD(T), and CCSD(T) levels of theories to understand their structural characteristics, thermodynamical properties, and bonding features. Electronic structure and spectroscopic features of the GeSi molecule have also been studied recently from ab initio based configuration interaction calculations.[17]

In this paper, we report PECs and spectroscopic properties of low-lying states of $GeSi^+$ from large scale MRDCI calculations which include pseudopotentials. Effects of the spin−orbit (SO) coupling on the electronic spectrum of $GeSi^+$ are studied for the first time. Transition probabilities of many dipole allowed and spin-forbidden transitions in $GeSi^+$ are calculated. Other properties like radiative lifetimes of the low-lying states and ionization energies for the ionization of the ground-state GeSi to the ground and low-lying excited states of $GeSi^+$ are estimated from the CI wave functions and compared with the available data.

II. Method of Calculations

The semicore average relativistic effective potentials (AREP) of Ge have been taken from Hurley et al.[18] The $3d^{10}4s^24p^2$ electrons of the atom are kept in the valence space, while the remaining 18 core electrons are described by means of AREP. For the silicon atom, $1s^22s^22p^6$ core electrons are replaced by the AREP of Pacios and Christriansen.[19] The primitive Gaussian basis functions (3s3p4d) of Ge, taken from Hurley et al.,[18] are augmented with two d polarization functions ($\zeta_d = 0.424$ and 0.15 a_0^{-2}) and a set of f polarization functions ($\zeta_f = 0.3458$ a_0^{-2}). The first two d-functions are contracted using the contraction coefficients of 0.062545 and 0.285448. The final contracted basis set for Ge is [3s3p5d1f]. The (4s4p) primitive Gaussian functions

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of Pacios and Christiansen[19] for Si are augmented with a number of diffuse and polarization functions. In the present calculations, we have added three s functions (ζ_s = 0.04525, 0.02715, and 0.0163 a_0^{-2}), two p functions (ζ_p = 0.06911 and 0.02499 a_0^{-2}), five d functions (ζ_d = 4.04168, 1.46155, 0.52852, 0.19112, and 0.06911 a_0^{-2}), and two f functions (ζ_f = 0.19112 and 0.06911 a_0^{-2}) from Matos et al.[20] The first two sets of d functions are contracted using the contraction coefficients of 0.054268 and 0.06973. Similarly, the two f functions are also contracted using the contraction coefficients of 0.29301 and 0.536102. The final contracted basis set for Si used in the present MRDCI calculations is [7s6p4d1f].

Self-consistent-field (SCF) calculations are carried out for the $(\sigma\pi^2)^4\Sigma^-$ state of $GeSi^+$ with 17 valence electrons at different internuclear distances ranging from 3.0 to 15.0 a_0 using C_{2v} subgroup. In the calculation, we have kept Ge at the origin and Si along the $+z$ axis. The symmetry adapted SCF-MOs are used as one electron basis for the generation of configurations in the subsequent CI calculations. The MRDCI method of Buenker and co-workers[21−26] with perturbative correction and energy extrapolation technique is used in the present CI calculations. The table-CI algorithm[27] has been employed to handle the open-shell configurations which appear because of the excitation process. The direct CI version[28] of the code has been used for getting energies and eigenfunctions. A set of reference configurations is chosen for the low-lying states of a given spin and spatial symmetry. We have optimized a few lowest roots for each symmetry of the ion. Single and double excitations from these references generate a large number of configurations with a maximum of the order of six million. However, using a configuration-selection threshold $T = 0.5\ \mu E_h$, the number of selected configurations remains below 200 000. Sums of the square of coefficients of the reference configurations for a few roots are kept above 0.90. Energy extrapolation method[21−23] is used to estimate energies at zero threshold. Effects of some of the higher order excitations are taken care by the Davidson correction.[29−31]

The SO CI calculations are performed by allowing all components of low-lying $\Lambda-\Sigma$ states to mix up. The spin−orbit operators,[18,19] compatible with AREP of both Ge and Si, are used for this purpose. The spin independent multireference CI wave functions are multiplied with appropriate spin functions, which transform as C_{2v}^2 irreducible representation. The diagonals of the spin included Hamiltonian matrix consist of energies of the $\Lambda-\Sigma$ CI calculations, while the off diagonals are calculated by using the SO operators and $\Lambda-\Sigma$ CI wave functions. The size of the secular equation of the E_1/E_2 block is 66 × 66 for some selected roots of $\Lambda-\Sigma$ symmetries of $GeSi^+$. Energies and wave functions are obtained from the diagonalization of the SO CI blocks.

PECs of both spin-independent and spin-included low-lying states of $GeSi^+$ are fitted into polynomials. The corresponding nuclear Schrödinger equations are then solved by Numerov-Cooley method[32] to obtain vibrational energies and vibrational wave functions for the bound states of the ion. Transition dipole moments for the pair of vibrational functions in a particular transition are computed. In the subsequent calculations, Einstein spontaneous emission coefficients, transition probabilities, and hence radiative lifetimes at different vibrational levels are estimated.

III. Results and Discussion

PECs and Spectroscopic Constants of $\Lambda-\Sigma$ States. Experimentally determined ionization energies of Ge and Si are known to be 7.90 and 8.15 eV, respectively. The difference of the two ionization energies is an estimation of the energy separation between the lowest two dissociation limits, $Ge^+(^2P_u)+Si(^3P_g)$ and $Ge(^3P_g)+Si^+(^2P_u)$. Therefore, the former limit is expected to lie lower than the latter by about 0.25 eV. MRDCI calculations of $GeSi^+$ at very large bond distances show an energy separation of 0.24 eV which agrees very well with the value obtained from the difference in IPs of the two atoms. Our calculated IP values of Ge and Si are 7.83 and 8.07 eV, respectively. Both $Ge^+(^2P_u)+Si(^3P_g)$ and $Ge(^3P_g)+Si^+(^2P_u)$ limits correlate with six doublets and six quartets of Σ^+, $\Sigma^-(2)$, $\Pi(2)$, and Δ symmetries of the $GeSi^+$ ion. PECs of all twenty four $\Lambda-\Sigma$ states of $GeSi^+$ dissociating into the lowest two asymptotes constructed from the MRDCI energies are shown in Figures 1 and 2 for quartets and doublets, respectively. Spectroscopic constants (T_e, r_e, ω_e, D_e) of 18 bound states of the ion are tabulated in Table 1.

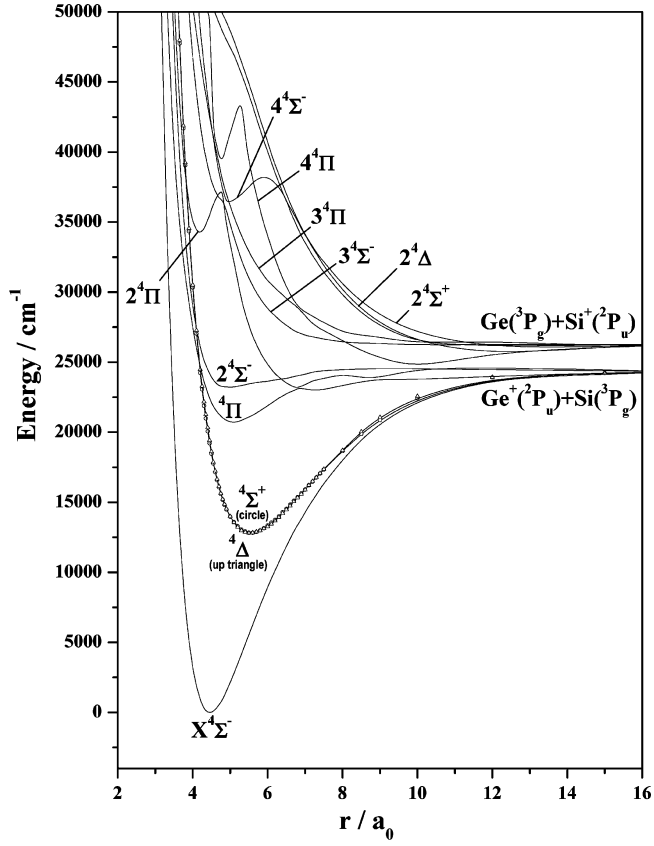

Figure 1. Potential energy curves of low-lying $\Lambda-\Sigma$ states of $GeSi^+$ for quartet spin multiplicity.

Like GeC^+, the ground state ($X^4\Sigma^-$) of $GeSi^+$ is generated from the neutral GeSi by removing an electron from the bonding σ orbital. The ground-state bond (r_e = 2.361 Å) of the ion is longer by about 0.018 Å than that of the neutral species. The computed vibrational frequency of the ground state of $GeSi^+$ is 360 cm^{-1}. The r_e and ω_e values in the present study are closer to the recent data reported by Wielgus et al.[16] at the CCSD(T) level, but at the MP2 level the bond is shorter by 0.02 Å. The MRDCI estimated r_e of Ueno et al.[15] is only 0.004 Å smaller than the present value, while Sefyani et al.[13] reported a much higher value. The ground state is dominated by the $2\sigma^2 3\sigma 1\pi^2$ configuration in which the doubly occupied 2σ MO is weakly antibonding and the singly occupied 3σ orbital is strongly bonding MO comprising s and p_z atomic orbitals of Ge and Si. The 1π MO is also a bonding combination of $p_{x/y}$ AOs of the two atoms. The leading configurations of all the low-lying states

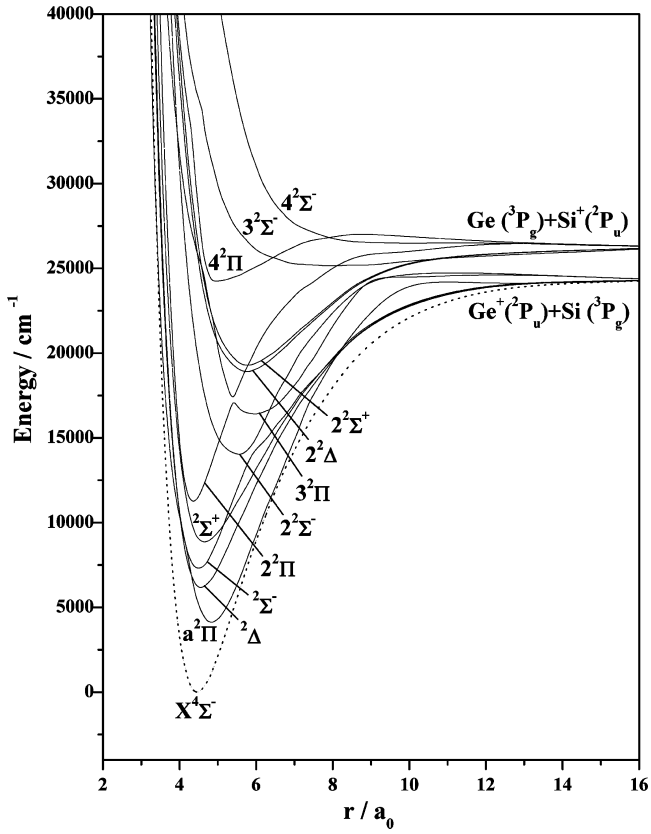

Figure 2. Potential energy curves of low-lying $\Lambda-\Sigma$ states of GeSi$^+$ for doublet spin multiplicity.

TABLE 1: Spectroscopic Constants of Low-lying $\Lambda-\Sigma$ States of GeSi$^+$

state	T_e/cm^{-1}	r_e/Å	ω_e/cm^{-1}	D_e/eV
X$^4\Sigma^-$	0	2.361	360	3.116
		2.389[a]	351[a]	
		2.357[b]		3.136[b]
		2.340[c]; 2.360[d]	381[c]; 361[d]	
a$^2\Pi$	4113	2.562	297	2.506
	4400[a]	2.569[a]	319[a]	
	4040[b]	2.539[b]		2.640[b]
		2.538[c]; 2.554[d]	331[c]; 307[d]	
$^2\Delta$	6174	2.414	319	2.250
	6400[a]	2.453[a]	310[a]	
$^2\Sigma^-$	7294	2.381	337	2.109
	7100[a]	2.385[a]	343[a]	
		2.368[c]; 2.377[d]	443[c]; 351[d]	
$^2\Sigma^+$	8857	2.460	284	1.917
	8400[a]	2.496[a]	307[a]	
2$^2\Pi$	11 245	2.306	466	1.620
	11 500[a]	2.313[a]	442[a]	
$^4\Sigma^+$	12 813	2.934	189	1.427
$^4\Delta$	12 815	2.934	189	1.427
2$^2\Sigma^-$	14 028	2.917	216	1.276
3$^2\Pi$	16 409	3.146	154	
2$^2\Delta$	18 904	3.053	177	0.913
2$^2\Sigma^+$	19 280	3.068	175	0.866
$^4\Pi$	20 713	2.700	191	0.447
2$^4\Sigma^-$	23 208	2.634	145	0.137
4$^2\Pi$	24 149	2.650	254	0.257
2$^4\Pi$	34 272	2.215	505	
4$^4\Sigma^-$	36 400	2.603	266	

[a] Reference 13. [b] Reference 15. [c] MP2, ref 16. [d] CCSD(T), ref 16.

of GeSi$^+$ are given in Table 2. The ground-state dissociation energy (D_e) of GeSi$^+$, computed in the absence of SO coupling, is about 3.116 eV, which agrees well with the earlier value reported by Ueno et al.[15]

TABLE 2: Composition of $\Lambda-\Sigma$ States of GeSi$^+$ at r_e

state	configuration (% contribution)
X$^4\Sigma^-$	$2\sigma^2 3\sigma 1\pi^2$ (76), $2\sigma^2 9\sigma 1\pi^2$ (2), $2\sigma^2 4\sigma 1\pi^2$ (1)
a$^2\Pi$	$2\sigma^2 3\sigma^2 1\pi$ (69), $2\sigma^2 3\sigma^2 2\pi$ (5), $2\sigma^2 1\pi^3$ (3)
$^2\Delta$	$2\sigma^2 3\sigma 1\pi^2$ (74), $2\sigma^2 3\sigma 1\pi 3\pi$ (5), $2\sigma^2 3\sigma 2\pi^2$ (2)
$^2\Sigma^-$	$2\sigma^2 3\sigma 1\pi^2$ (77), $2\sigma^2 9\sigma 1\pi^2$ (2), $2\sigma^2 4\sigma 1\pi^2$ (1)
$^2\Sigma^+$	$2\sigma^2 3\sigma 1\pi^2$ (69), $2\sigma^2 3\sigma 1\pi 2\pi$ (10)
2$^2\Pi$	$2\sigma^2 1\pi^3$ (59), $2\sigma^2 3\sigma^2 1\pi$ (17), $2\sigma^2 1\pi 2\pi^2$ (4), $2\sigma^2 1\pi^2 2\pi$ (2)
$^4\Sigma^+$	$2\sigma^2 3\sigma 1\pi 2\pi$ (82)
$^4\Delta$	$2\sigma^2 3\sigma 1\pi 2\pi$ (82)
2$^2\Sigma^-$	$2\sigma^2 3\sigma 1\pi 2\pi$ (81), $2\sigma^2 3\sigma 1\pi^2$ (1)
3$^2\Pi$	$2\sigma^2 1\pi^2 2\pi$ (68), $2\sigma^2 1\pi 2\pi^2$ (10), $2\sigma^2 1\pi^3$ (8)
2$^2\Delta$	$2\sigma^2 3\sigma 1\pi 2\pi$ (82)
2$^2\Sigma^+$	$2\sigma^2 3\sigma 1\pi 2\pi$ (82)
$^4\Pi$	$2\sigma^2 1\pi^2 2\pi$ (74), $2\sigma^2 1\pi 2\pi^2$ (8)
2$^4\Sigma^-$	$2\sigma^2 3\sigma 1\pi 2\pi$ (40), $2\sigma^2 3\sigma 1\pi^2$ (17), $2\sigma 3\sigma^2 1\pi^2$ (10), $2\sigma^2 3\sigma 2\pi^2$ (7)
4$^2\Pi$	$2\sigma^2 1\pi^2 2\pi$ (70), $2\sigma^2 3\sigma^2 2\pi$ (5), $2\sigma^2 1\pi 2\pi^2$ (4)
2$^4\Pi$	$2\sigma 3\sigma 1\pi^3$ (66), $2\sigma^2 1\pi^2 2\pi$ (11)
4$^4\Sigma^-$	$2\sigma 3\sigma^2 1\pi^2$ (34), $2\sigma^2 8\sigma 1\pi^2$ (17), $2\sigma 3\sigma^2 1\pi 2\pi$ (8)

The first excited state, a$^2\Pi$ is lying only 4113 cm^{-1} above the ground state. It is comparable with T_e values obtained in the previous calculations.[13,15] The Ge−Si bond in this state is substantially longer ($r_e = 2.562$ Å) than the ground-state bond. A loss of an electron from the strongly bonding 1π MO makes the a$^2\Pi$ state less binding. However, MP2 studies of Wielgus et al.[16] predicted a much shorter r_e for the a$^2\Pi$ state of the ion. The next three doublets, $^2\Delta$, $^2\Sigma^-$, and $^2\Sigma^+$ of GeSi$^+$ originating from the $2\sigma^2 3\sigma 1\pi^2$ configuration same as that of the ground state, correlate with the Ge$^+$(^{2}P$_u$)+Si(^{3}P$_g$) limit. Spectroscopic constants of $^2\Sigma^-$ calculated in the present study are comparable with those obtained by Sefyani et al.[13] But its r_e and ω_e values calculated at the MP2 and CCSD(T) levels by Wielgus et al.[16] are somewhat different from the present results. As seen in Figure 2, there is an avoided crossing of the $^2\Sigma^-$ state with its higher root around the bond distance of 5.9 a_0. Although the extent of configuration mixing in the FC region of these two curves is small, the adiabatic curve of the 2$^2\Sigma^-$ state is fitted for the estimation of spectroscopic constants. The 2$^2\Sigma^-$ state, which is characterized by $2\sigma^2 3\sigma 1\pi 2\pi$, has a transition energy of about 14 000 cm^{-1} at equilibrium. The computed bond length is also found to be large, as expected from the composition of the state.

The potential minimum of the $^2\Sigma^+$ state is located 8857 cm^{-1} above the ground state, which is 457 cm^{-1} larger than the previous value.[13] The computed equilibrium bond length of GeSi$^+$ in the $^2\Sigma^+$ state is shorter than the earlier MRCI estimated value[13] by 0.036 Å, while its vibrational frequency is smaller by 23 cm^{-1}. At equilibrium, there is at least 10% contribution of the $2\sigma^2 3\sigma 1\pi 2\pi$ configuration in which 2π is strongly antibonding type MO. The second root of $^2\Sigma^+$, which dissociates into Ge(^{3}P$_g$)+Si$^+$(^{2}P$_u$), interacts strongly with the first one. This has been confirmed from the MRDCI wave functions of the lowest two roots of $^2\Sigma^+$ in the longer bond length region where the 2$^2\Sigma^+$ state is dominated by $2\sigma^2 3\sigma 1\pi^2$. The transition energy of 2$^2\Sigma^+$ estimated from the adiabatic PEC is about 19 280 cm^{-1}. Because of the occupancy of the antibonding 2π orbital, the bonding nature of the 2$^2\Sigma^+$ state is somewhat different.

The 2$^2\Pi$ state of GeSi$^+$ lies just above $^2\Sigma^+$ with a separation of 2388 cm^{-1}. It has a much shorter bond length ($r_e = 2.306$ Å) compared to the other low-lying doublets. The state originates from a $3\sigma \rightarrow 1\pi$ excitation in which 3σ is weakly antibonding and 1π is strongly bonding. Thus the bonding character in the 2$^2\Pi$ state increases to a small extent. There is a strong mixing

of $2^2\Pi$ with its lower root in the shorter bond length region, which is reflected in the compositions of the two roots. Even at r_e, the $2^2\Pi$ state has a 17% contribution of $2\sigma^2 3\sigma^2 1\pi$, which is the leading configuration of $a^2\Pi$. As a result, the vibrational frequency estimated from the adiabatically fitted curve of $2^2\Pi$ is substantially large ($\omega_e = 466$ cm^{-1}). The diabatic curve of $2^2\Pi$ correlates with the Ge+Si$^+$ limit. Another avoided crossing with the third root of $^2\Pi$ at 5.4 a_0 is noted in Figure 2. In the FC region of the $3^2\Pi$ state, the dominant configuration ($2\sigma^2 1\pi^2 2\pi$) is mixed up with $2\sigma^2 1\pi 2\pi^2$ and $2\sigma^2\ 1\pi^3$ (Table 2). The PEC of $3^2\Pi$ is relatively broad and the minimum is located at a longer bond length ($r_e = 3.146$ Å). The potential minimum of the $4^2\Pi$ state has been predicted at 2.65 Å with a transition energy of about 24 150 cm^{-1}. The state dissociates into Ge(^3P_g)+Si$^+$(^2P_u) with a binding energy less than 0.25 eV. Spectroscopic constants and the nature of the PEC of the $2^2\Delta$ state are similar to those of $2^2\Sigma^+$. The energy separation between these two states is only 384 cm^{-1}. Both the states originate from the same configuration and dissociate into the same limit. The remaining two doublets, namely $3^2\Sigma^-$ and $4^2\Sigma^-$ are repulsive.

Two nearly degenerate quartets, $^4\Delta$ and $^4\Sigma^+$ are predicted to be 12 800 cm^{-1} above the ground state. They originate from the same configuration with almost the same contribution and the configuration includes a singly occupied 2π orbital which is strongly antibonding in nature. Neither of the two quartets is suitable for dipole allowed transitions to the ground state. Both $^4\Delta$ and $^4\Sigma^+$ states have the same spectroscopic constants ($r_e =$ 2.934 Å and $\omega_e = 189$ cm^{-1}). The next important quartet, $^4\Pi$ has a transition energy of 20 713 cm^{-1} and the state arises mainly due to a $3\sigma\rightarrow 2\pi$ excitation of the ground state. However, another configuration, $2\sigma^2 1\pi 2\pi^2$ contributes to a small extent. Although the excited state is not strongly bound, there is a possibility of a $^4\Pi$-$X^4\Sigma^-$ transition in the 20 000−21 000 cm^{-1} region.

Three higher roots of $^4\Pi$ are mixed up in the different regions of their PECs. This is reflected in the avoided crossings of these states. A very shallow global minimum around 7 a_0 appears in the diabatic curve of the second root leading to Ge$^+$(^2P_u)+Si(^3P_g). However, to the left of the shallow minimum there is a barrier of height 8.3 kcal mol^{-1} beyond which a very steep minimum exists at 2.215 Å. We have labeled this short-distant minimum as $2^4\Pi$. The existence of the barrier is a result of the avoided crossings which are confirmed from the compositions of CI wave functions of the corresponding states. The $2^4\Pi$ state around 2.215 Å is dominated by a configuration, $2\sigma 3\sigma 1\pi^3$, while around the global minimum, the leading configuration is $2\sigma^2 3\sigma 4\sigma 1\pi$.

The PEC of the $2^4\Sigma^-$ state shows a shallow minimum at r_e = 2.634 Å. It is composed of a leading configuration, $2\sigma^2 3\sigma 1\pi 2\pi$(40%) and three other configurations, namely $2\sigma^2 3\sigma 1\pi^2$, $2\sigma 3\sigma^2 1\pi^2$, and $2\sigma^2 3\sigma 2\pi^2$ having significant contributions. The $2^4\Sigma^- - X^4\Sigma^-$ transition in the region 23 000−24 000 cm^{-1} is expected to be strong. The higher roots, $3^4\Sigma^-$ and $4^4\Sigma^-$ undergo an avoided crossing around 4.85 a_0. The diabatic potential well for the $4^4\Sigma^-$ state of GeSi$^+$ is fitted for the calculation of spectroscopic constants. The potential minimum of $4^4\Sigma^-$ is located at 2.603 Å with a fitted T_e and ω_e of 36 400 and 266 cm^{-1}, respectively. The PEC of the state exhibits a barrier of 4.9 kcal mol^{-1} around the bond length of 6 a_0 before dissociating into Ge(^3P_g)+Si$^+$(^2P_u) through a repulsive curve. The $3^4\Sigma^-$ state, which is composed of $2\sigma^2 3\sigma 2\pi^2$, is repulsive dissociating into the same limit.

Spectroscopic Properties of Ω States. The SO coupling does not have a large effect on the structure and spectroscopic properties of GeSi$^+$. However, the lowest dissociation limit, Ge$^+$(^2P_u)+Si(^3P_g) splits into six closely spaced asymptotes which correlate with 27 states of the GeSi$^+$ ion with Ω = 1/2, 3/2, 5/2, and 7/2 symmetries. The overall SO splitting of this dissociation limit reported in the Atomic Spectral Data Table[34] is 1966 cm^{-1} which compares well with the value of 1988 cm^{-1} calculated from the present MRDCI study. In the SO calculations, we have included all 24 Λ−Σ doublets and quartets which correlate with the lowest two dissociation limits, Ge$^+$+Si and Ge+Si$^+$. The computed PECs of the low-lying Ω states of GeSi$^+$ are shown in Figures 3−5. The zero-field splitting of the ground state is only 12 cm^{-1}. Spectroscopic constants of $X^4\Sigma^-_{1/2}$ and $X^4\Sigma^-_{3/2}$ do not change much (Table 3) and the ground-state dissociation energy is decreased by 0.1 eV.

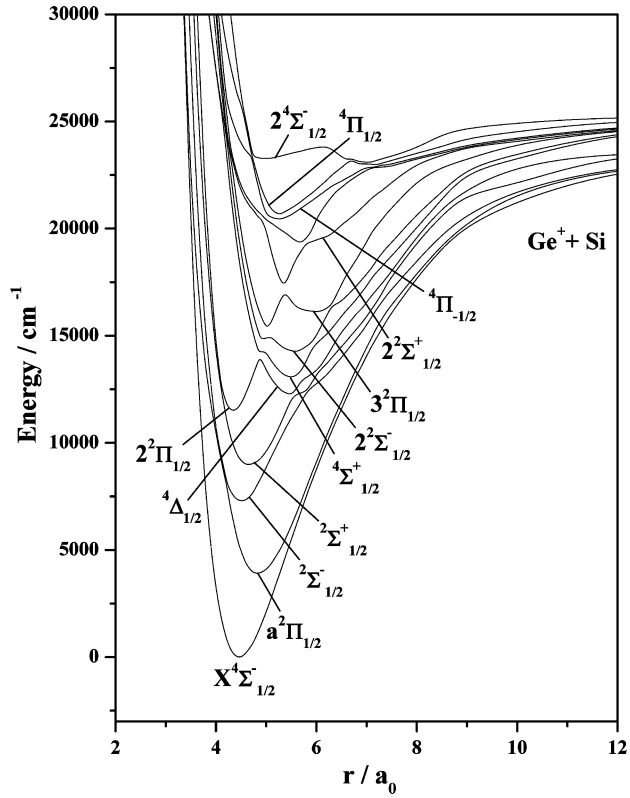

Figure 3. Potential energy curves of low-lying Ω states of GeSi$^+$ for Ω =1/2.

The $a^2\Pi$ state splits into 1/2 and 3/2 with a separation of 447 cm^{-1}. The SO interaction makes no change in their spectroscopic constants. A similar situation is obtained for the two components of $^2\Delta$, but the $^2\Delta_{5/2}-{}^2\Delta_{3/2}$ splitting is relatively small. The PECs of $a^2\Pi_{3/2}$ and $^2\Delta_{3/2}$ as shown in Figure 4 undergo a weak avoided crossing in the region 3.8−4.2 a_0. The spin components of $^2\Sigma^-$ and $^2\Sigma^+$ exhibit several avoided crossings in their PECs. As a result, their r_e values are increased by 0.01 Å, while the vibrational frequencies change only marginally. The energy separation between the two spin states of $2^2\Pi$ is estimated to be 352 cm^{-1} with the 3/2 component lying lower. The $^4\Delta$ state, which splits into four components in a regular order, has an overall splitting of 1235 cm^{-1}.

The $^4\Sigma^+_{3/2}$ and $^4\Sigma^+_{1/2}$ states undergo many avoided crossings as shown in Figures 3 and 4. Although SO splitting is only 216 cm^{-1}, the estimated r_e and ω_es of these states vary to some extent. At the potential minimum, the $^4\Sigma^+_{1/2}$ component is composed of $^4\Sigma^+$(77%) and $2^2\Sigma^-$(19%), while the other component, $^4\Sigma^+_{3/2}$ remains almost pure. The SO splitting of $3^2\Pi$ is found to be in a regular order with a maximum separation of

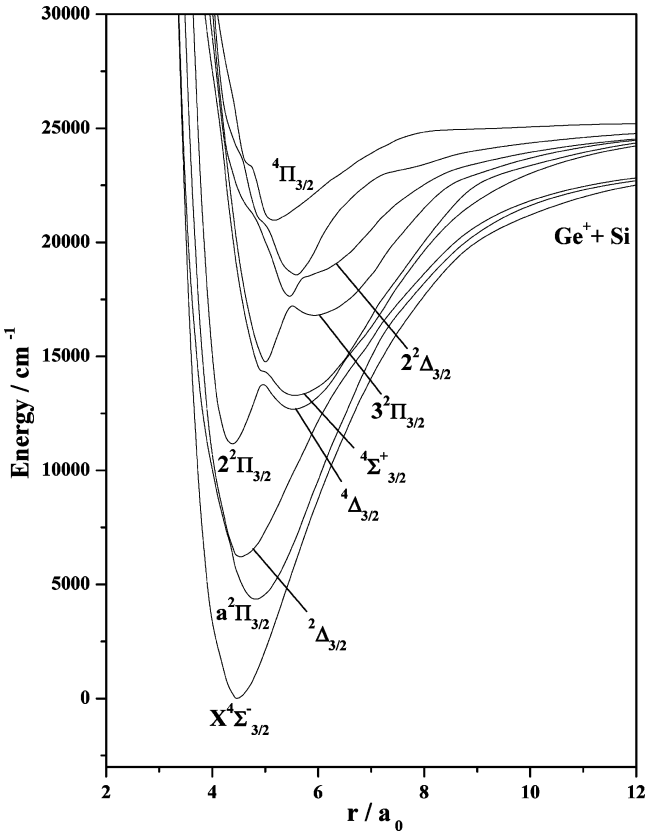

Figure 4. Potential energy curves of low-lying Ω states of $GeSi^+$ for $\Omega = 3/2$.

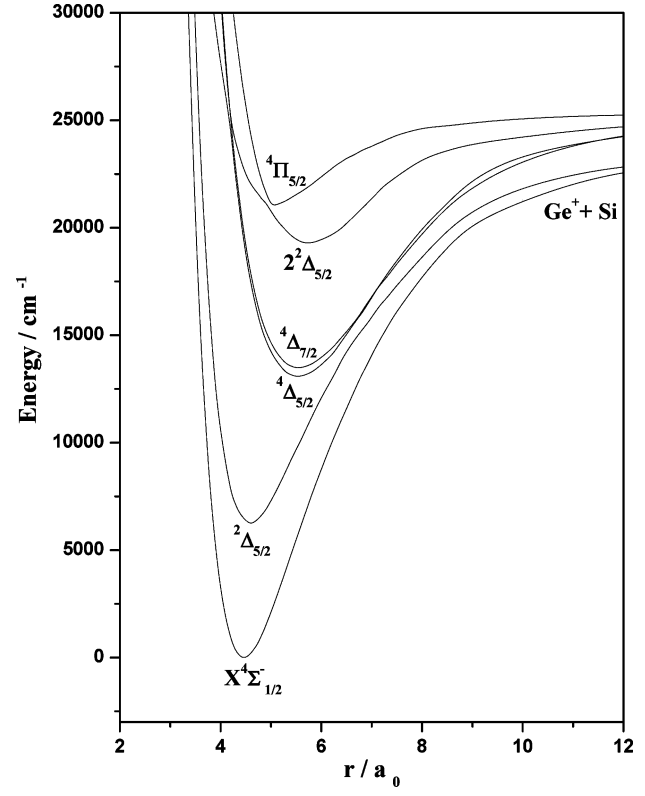

Figure 5. Potential energy curves of low-lying Ω states of $GeSi^+$ for $\Omega = 5/2$ and 7/2.

685 cm^{-1}. In general, several avoided crossings among the Ω states of 1/2 and 3/2 symmetries in the 11 000−22 000 cm^{-1} region make their potential curves a bit complex. However, PECs of 5/2 states are less contaminated. A shoulder appears in the PEC of $2^2\Delta_{5/2}$ due to a weak avoided crossing with the $^4\Pi_{5/2}$ state. The lowest $^4\Pi$ state also splits in a regular order with an overall splitting of 590 cm^{-1}. The calculations show that $^4\Pi_{1/2}$ and $^4\Pi_{-1/2}$ states mix up with $2^2\Sigma^+_{1/2}$.

TABLE 3: Spectroscopic Constants of Low-lying Ω States of $GeSi^+$

state	T_e/cm^{-1}	r_e/Å	ω_e/cm^{-1}
$X^4\Sigma^-_{1/2}$	0	2.36	363
$X^4\Sigma^-_{3/2}$	12	2.36	359
$a^2\Pi_{1/2}$	3903	2.56	298
$a^2\Pi_{3/2}$	4350	2.56	298
$^2\Delta_{3/2}$	6208	2.41	330
$^2\Delta_{5/2}$	6275	2.44	308
$^2\Sigma^-_{1/2}$	7280	2.39	327
$^2\Sigma^+_{1/2}$	8981	2.47	290
$2^2\Pi_{3/2}$	11 158	2.32	470
$2^2\Pi_{1/2}$	11 510	2.30	440
$^4\Delta_{1/2}$	12 246	2.93	192
$^4\Delta_{3/2}$	12 668	2.93	199
$^4\Sigma^+_{1/2}$	13 064	2.91	285
$^4\Delta_{5/2}$	13 081	2.93	189
$^4\Sigma^+_{3/2}$	13 280	2.95	185
$^4\Delta_{7/2}$	13 481	2.94	187
$2^2\Sigma^-_{1/2}$	14 271	2.95	205
$3^2\Pi_{1/2}$	16 106	3.16	168
$3^2\Pi_{3/2}$	16 791	3.14	168
$2^2\Delta_{3/2}$	18 476	3.01	185
$2^2\Delta_{5/2}$	19 288	3.04	168
$2^2\Sigma^+_{1/2}$	19 315	3.07	163
$^4\Pi_{-1/2}$	20 448	2.75	170
$^4\Pi_{1/2}$	20 683	2.80	261
$^4\Pi_{3/2}$	20 900	2.70	249
$^4\Pi_{5/2}$	21 038	2.67	226

Transition Moments and Radiative Lifetimes. Transition dipole moments of four quartet−quartet and four doublet−doublet transitions for $GeSi^+$ are computed from the Λ−Σ CI calculations. Figure 6 shows transition moment curves as a function of the internuclear distance. The transition moment for $2^4\Sigma^--X^4\Sigma^-$ increases rapidly and reaches a maximum value of 1.05 ea_0 at a bond distance of 5.15 a_0. However, it smoothly decreases to a negligible value in the longer bond distance region. Therefore, the $2^4\Sigma^-−X^4\Sigma^-$ transition is expected to occur in the 23 000−23 500 cm^{-1} region with a high transition probability. The computed radiative lifetimes of various dipole allowed and spin-forbidden transitions at $v' = 0-2$ levels are reported in Table 4. The lifetime for $2^4\Sigma^-−X^4\Sigma^-$ is predicted to be around 52 ns at $v' = 0$ and it increases with v'. Transition moments for the $4^4\Sigma^-−X^4\Sigma^-$ transition are very large at the shorter bond distances but it rapidly diminishes and passes through zero at 5.1 a_0. As a result, the transition probability for this transition is smaller than that for $2^4\Sigma^-−X^4\Sigma^-$. The computed radiative lifetime for $4^4\Sigma^-−X^4\Sigma^-$ is 89.2 ns at the lowest vibrational level and it decreases with v'. The remaining two transitions, $^4\Pi−X^4\Sigma^-$ and $2^4\Pi−X^4\Sigma^-$ are very weak due to their smaller transition moments and the estimated lifetimes are of the order of millisecond or slightly less.

Among the four doublet−doublet transitions reported here, $4^2\Pi−a^2\Pi$ has the strongest transition probability. In the FC region, transition moment for this transition has got a maximum value of 0.94 ea_0. The partial radiative lifetime for this transition is predicted to be 1−3 μs at $v' = 0$. The remaining three transitions, $^2\Delta−a^2\Pi$, $^2\Sigma^-−a^2\Pi$, and $^2\Sigma^+−a^2\Pi$ are, however, less probable. Transition moment curves for both $^2\Delta−a^2\Pi$ and $^2\Sigma^-−a^2\Pi$ look similar with a broad maximum in the FC region (Figure 6). The largest transition moment value for $^2\Delta−a^2\Pi$ is

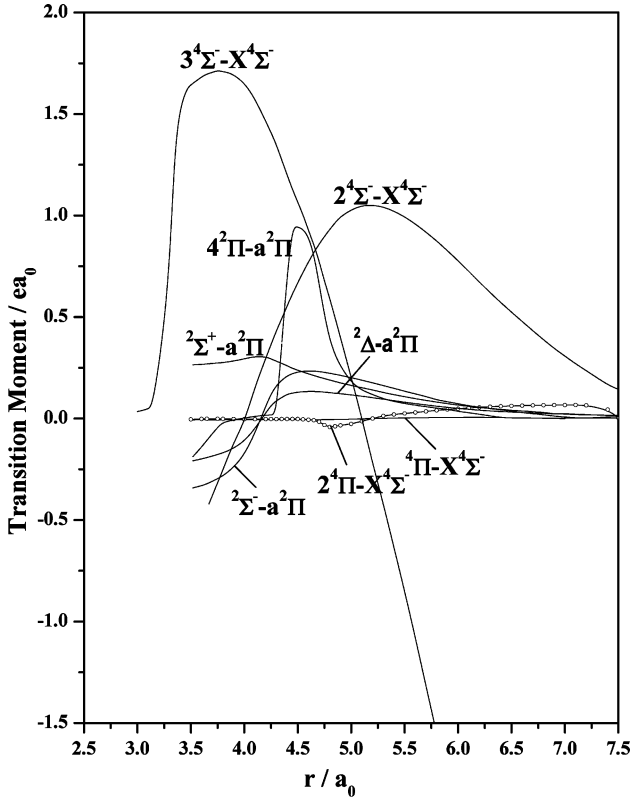

Figure 6. Transition dipole moment curves of some low-lying doublet−doublet and quartet−quartet transitions of $GeSi^+$.

TABLE 4: Radiative Lifetime(s) of Some Excited States of $GeSi^+$ [a]

	partial lifetime of the upper state		
transition	$v' = 0$	$v' = 1$	$v' = 2$
$2^4\Sigma^- - X^4\Sigma^-$	5.18(−8)	5.89(−8)	6.82(−8)
$4^4\Sigma^- - X^4\Sigma^-$	8.92(−8)	6.44(−8)	4.31(−8)
$^4\Pi - X^4\Sigma^-$	1.73(−2)	7.44(−3)	6.31(−3)
$2^4\Pi - X^4\Sigma^-$	6.49(−3)		
$^2\Delta - a^2\Pi$	7.39(−3)	4.82(−3)	3.73(−3)
$^2\Sigma^- - a^2\Pi$	7.66(−4)	5.10(−4)	3.79(−4)
$^2\Sigma^+ - a^2\Pi$	1.28(−4)	1.33(−4)	1.38(−4)
$4^2\Pi - a^2\Pi$	1.31(−6)	9.36(−7)	
$^2\Sigma^-_{1/2} - X^4\Sigma^-_{1/2}$	1.31(−2)	1.39(−2)	1.35(−2)
$^2\Sigma^+_{1/2} - X^4\Sigma^-_{1/2}$	9.77(−2)	1.42(−1)	1.86(−1)
$2^2\Pi_{1/2} - X^4\Sigma^-_{1/2}$	1.10(−1)		
$^2\Delta_{3/2} - X^4\Sigma^-_{1/2}$	4.33(−2)	3.88(−2)	3.81(−2)
$2^2\Pi_{3/2} - X^4\Sigma^-_{1/2}$	1.01(−2)	8.80(−3)	
$^2\Delta_{3/2} - X^4\Sigma^-_{3/2}$	5.49(−2)	4.43(−2)	3.25(−2)
$^2\Sigma^-_{1/2} - X^4\Sigma^-_{3/2}$	6.29(−3)	6.00(−3)	6.10(−3)
$^2\Sigma^+_{1/2} - X^4\Sigma^-_{3/2}$	1.05(−2)	8.83(−3)	8.11(−3)
$^2\Delta_{5/2} - X^4\Sigma^-_{3/2}$	2.06(−2)	1.85(−2)	1.77(−2)

[a] Values in parentheses are power to base 10.

nearly half that for $^2\Sigma^- - a^2\Pi$, consequently the estimated lifetime for the former transition is nearly 10 times longer than that for the latter one.

Five spin-forbidden transitions to $X^4\Sigma^-_{1/2}$ and another four to $X^4\Sigma^-_{3/2}$ are also studied here. All of them are weak and their transition moments are not more than 0.015 ea_0. The nature of the transition moment curves for these transitions is shown in Figure 7. The computed partial lifetimes (Table 4) for the spin-forbidden transitions are not less than a millisecond. At $v' = 0$, the shortest lifetime of 6.29 ms has been predicted for the $^2\Sigma^-_{1/2} - X^4\Sigma^-_{3/2}$ transition, while the longest one is for $^2\Delta_{3/2} - X^4\Sigma^-_{3/2}$.

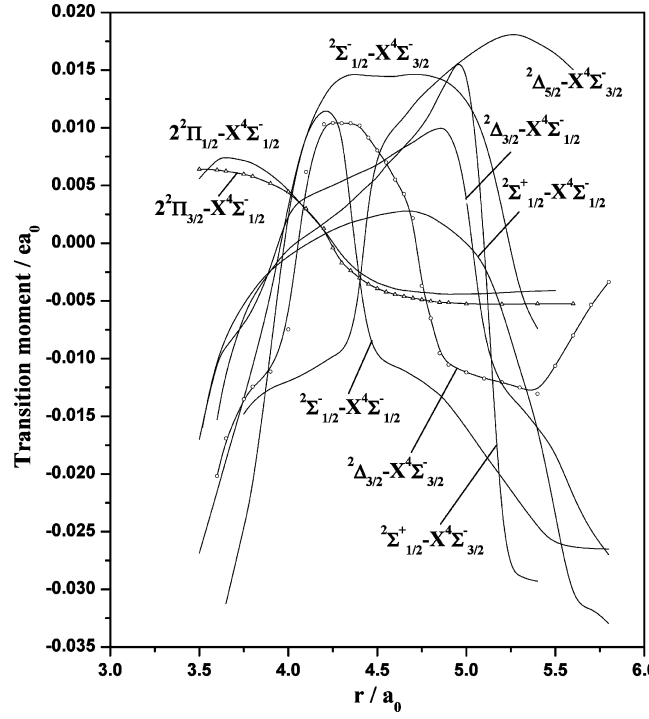

Figure 7. Transition dipole moment curves of some spin-forbidden transitions of $GeSi^+$.

TABLE 5: Vertical and Adiabatic Ionization Energies of GeSi

state	VIE/eV	AIE/eV
$X^4\Sigma^-$	7.91	7.47
	7.414[a]	
	7.518[b]	7.514[b]
	7.52[c]; 7.63[d]	
	8.2 ± 0.3[e]	
	7.2 ± 0.5[f]	
$a^2\Pi$	8.18	7.98
	8.017[b]	8.008[b]
	8.17[c]; 8.12[d]	
$^2\Delta$	8.26	8.24
$^2\Sigma^-$	8.39	8.38
	8.12[c]; 8.05[d]	
$^2\Sigma^+$	8.62	8.57
$2^2\Pi$	8.87	8.88
$^4\Delta$	9.94	9.06
$^4\Sigma^+$	10.04	9.11
$2^2\Sigma^-$	10.02	9.21
$3^2\Pi$	10.72	9.50
$2^2\Delta$	10.72	9.81
$2^2\Sigma^+$	10.88	9.86
$^4\Pi$	10.28	10.04
$2^4\Sigma^-$	10.49	10.35
$4^2\Pi$	11.21	10.47
$2^4\Pi$	11.84	11.72
$4^4\Sigma^-$	12.27	11.91

[a] Reference 13. [b] Reference 15. [c] MP2, ref 16. [d] CCSD(T), ref 16. [e] Reference 7. [f] Reference 33.

Vertical and Adiabatic Ionization Energies. Vertical (VIEs) and adiabatic ionization energies (AIEs) of GeSi to the ground and low-lying excited states of the ion have been computed from the differences in the CI energies of the neutral and ionic species at the same level of MRDCI calculations. In Table 5, we have listed VIEs and AIEs for the ionization to all 17 Λ−Σ states of $GeSi^+$. For the calculations of VIEs, we have taken the ground-state bond length of 2.343 Å for GeSi. The ionization to the ground-state $GeSi^+$ involves a removal of 3σ electron and in

the present calculations the VIE is found to be 7.91 eV. The mass spectrometric appearance potentials reported by Drowart et al.[7] is 8.2 ± 0.3 eV, but a somewhat smaller value of 7.2 ± 0.5 eV has been obtained in a more recent study.[33] However, VIEs of 7.52 and 7.63 eV,[16] obtained from MP2 and CCSD(T) calculations[16] are in better agreement with the present values, while those calculated at other levels[13,15] vary between 7.4 and 7.6 eV. The AIE for the ionization of $GeSi(X^3\Sigma^-)$ to $GeSi^+(X^4\Sigma^-)$ matches well with the value reported by Ueno et al.[15] The computed VIE for the ionization of the ground-state GeSi to the $a^2\Pi$ state of the ion is 8.18 eV which is comparable with the MP2 calculated value of 8.17 eV, while the CCSD(T) calculation predicted a somewhat smaller VIE value. The corresponding AIE value is about 8 eV which is in good agreement with the previous theoretical value. The VIE for the ionization to the $^2\Sigma^-$ state is slightly overestimated compared to either the MP2 or CCSD(T) calculated value.

IV. Conclusion

MRDCI method, which includes relativistic effects and SO coupling, has been employed to study PECs, spectroscopic constants, and transition properties for the ground and low-lying electronic states of $GeSi^+$ within 5 eV of energy. PECs of at least 24 $\Lambda-\Sigma$ states, which correlate with the two close lying dissociation limits, $Ge^+ + Si$ and $Ge + Si^+$, are constructed. The ground state ($X^4\Sigma^-$) of $GeSi^+$ is mainly represented by the $.\sigma\pi^2$ configuration. Its bond length is 0.018 Å longer than that of the neutral species. The ground-state dissociation energy of $GeSi^+$ is 3.116 eV in the absence of any SO coupling. The lowest doublet belongs to $a^2\Pi$ whose equilibrium bond length is at least 0.2 Å longer than that of the ground state. Two nearly degenerate quartets, $^4\Delta$ and $^4\Sigma^+$ are approximately located 12 800 cm^{-1} above the ground state. Both the states are predicted to have the same spectroscopic properties. The overall SO coupling is not large enough to change the structural features of $GeSi^+$ significantly. The largest overall SO splitting of 1235 cm^{-1} has been reported for the $^4\Delta$ state of the ion. $2^4\Sigma^- - X^4\Sigma^-$ and $4^4\Sigma^- - X^4\Sigma^-$ transitions are expected to have strong transition probabilities with the estimated partial radiative lifetimes of 52 and 89 ns, respectively at $v' = 0$. All the spin-forbidden transitions are fairly weak and the lifetimes are computed to be of the order of millisecond or more. The computed VIEs and AIEs for the ionizations of the ground-state GeSi to the ground and low-lying excited states of the ion agree with some of the previously calculated data.

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