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Electronic states and spectroscopic properties of GeSi

Susmita Chakrabarti, Kalyan Kumar Das *

Department of Chemistry, Physical Chemistry Section, Jadavpur University, 188, Raja S.C. Mallik Road, Jadavpur, Kolkata 700 032, India

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ABSTRACT

Electronic structure and spectroscopy of the GeSi molecule have been investigated by performing ab initio based multireference configuration interaction calculations. Potential energy curves of 29 Λ-S states of singlet, triplet, and quintet spin multiplicities have been constructed. Spectroscopic constants of 24 bound states within 36 000 cm^{-1} are reported and compared with the available data. The calculated dissociation energy of GeSi in the ground state is 2.80 eV. Effects of the spin–orbit coupling on the spectroscopic properties of the molecule have been found to be small. However, the computed zero-field-splitting of the ground state compares well with the earlier prediction. Transitions such as $2^3\Sigma^-$–$X^3\Sigma^-$, $3^3\Sigma^-$–$X^3\Sigma^-$, $4^3\Pi$–$A^3\Pi$, $5^3\Pi$–$A^3\Pi$ etc. are relatively strong. Radiative lifetimes for several dipole allowed and spin-forbidden transitions are calculated. The estimated lifetimes of the $2^3\Sigma^-$, $3^3\Sigma^-$, and $5^3\Pi$ states are about 109, 33, and 62 ns, respectively. Dipole moments of most of the low-lying states of GeSi are also reported.

1. Introduction

Small molecules composed of group IV atoms are important from the experimental point of view due to their applications in the optoelectronics and semiconductor industries [1–9]. The chemical vapor deposition technique is used to form semiconductor films with these materials. These molecules are also used in surface growth processes and their possible existence in interstellar space has made them the subject of many researches in the past. It is important to study the nature of chemical bonding to understand the chemical and physical properties of these semiconductor materials, so that the quality of these materials can be improved. The element germanium possesses very high electron and hole mobilities which make it a viable alternative for high speed microelectronic chips. Therefore, studies of the electronic structure and spectroscopic aspects of gaseous intragroup-IV molecules like SiC, GeC, GeSi, and their ions have become of interest. The binary heterostructure $\mathrm{Si/Si_{1-x}Ge_x}$ has produced a new generation of high performance heterojunction bipolar transistors, field effect transistors, and infrared detectors [10].

Among the heteronuclear diatomic molecules of group-IV, SiC has been studied extensively, both experimentally as well as theoretically [11–17]. On the other hand, molecules like GeC and GeSi are seldom studied, possibly because of the experimental difficulties in preparing their gas-phase samples as in SiC [18]. Drowart et al. [19,20] first studied mass spectrometry of inter-group IV B molecules. These authors reported the dissociation energies of GeC and GeSi molecules as 4.72 ± 0.22 and 3.08 ± 0.22 eV, respectively, using Knudsen effusion mass spectrometric technique. Sefyani et al. [21] have performed self-consistent-field/multireference configuration interaction calculations on GeC using pseudo potentials. They studied spectroscopic parameters of the ground state ($X^3\Pi$) and five low-lying excited states of GeC. Similar calculations have been carried out by Shim et al. [22] on the lowest $X^3\Pi$, $^3\Sigma^-$, $^1\Sigma^+$, $^1\Pi$, and $^1\Delta$ states of the germanium carbide molecule.

Recently, structural and electronic properties of semiconductor binary microclusters A_mB_n (A,B = Si,Ge,C) have been investigated by Li et al. [23] using B3LYP-DFT calculations. They have predicted that the SiC, GeC, and GeSi molecules all have triplet ground state with bond lengths of 1.71, 1.80, and 2.22 Å and bond energies of 4.36, 3.83, and 2.90 eV, respectively. The infrared spectra of the GeSi and SnSi molecules in argon matrices at 4 K have been recorded by Li et al. [24] for frequencies up to 3000 cm^{-1}. They have also observed the $X'^3\Pi \leftarrow X^3\Sigma^-$ transition as a vibrational progression. The lowest frequency band in this progression for GeSi begins at about 798 cm^{-1} with an average vibrational spacing of 430 cm^{-1}. Apart from the Knudsen mass spectrometric work, the matrix isolation study is the only existing experimental work on GeSi.

Andzelm et al. [25] first reported the spectroscopic constants and electronic structure of diatomic molecules like $\mathrm{Si_2}$, $\mathrm{Ge_2}$, $\mathrm{Sn_2}$, SiGe, SiSn, and GeSn in their ground and low-lying excited states from local spin-density calculations. Potential energy curves for the ground and the low-lying $^3\Pi$, $^1\Sigma^+$, and $^1\Delta$ states were reported. The computed D_e of the ground state of SiGe was found to be 3.79 eV. Sefyani et al. [26] have performed ab initio calculations at the multireference configuration interaction level for the

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* Corresponding author. Fax: +91 33 2414 6223.
E-mail address: kkdas@chemistry.jdvu.ac.in (K.K. Das).

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energies and structural properties of the valence electronic states of the GeSi molecule below 30 000 cm^{-1}. Radiative lifetimes for three transitions, $2^3\Sigma^- \rightarrow X^3\Sigma^-$, $3^3\Sigma^- \rightarrow X^3\Sigma^-$, and $5^3\Pi \rightarrow X^3\Sigma^-$ of GeSi were computed by these authors. In a related calculation, spectroscopic properties of six lowest states of GeSi$^+$ have been reported by Sefyani et al. [27], supplementing the previous results on the neutral species.

Recently, Sari et al. [28] have thoroughly studied the lowest two states, namely $^3\Sigma^-$ and $^3\Pi$, of GeC and GeSi using the highly correlated coupled-cluster level of theory. They have also included scalar relativistic corrections and core–valence correlation in their calculations. A large discrepancy of about 18 kcal/mol has been reported between the theoretical and experimental dissociation energy of GeC. Very recently, the lowest few states of GeC, GeSi, and their monopositive ions have been theoretically investigated by Ueno et al. [29]. They have used the MRCI method and the augmented correlation-consistent polarized valence quadruple zeta type of basis functions. Franck–Condon factors and ionization energies for both GeC → GeC$^+$ and GeSi → GeSi$^+$ have been reported.

The present article is aimed at the theoretical studies of the potential energy curves and spectroscopic properties of low-lying electronic states of GeSi by using multireference singles and doubles CI (MRDCI) methodology, taking into account relativistic effects through the effective core potentials. Spin–orbit coupling has been included for the first time in GeSi extensively. Other properties, such as transition probabilities of dipole allowed and spin-forbidden transitions, radiative lifetimes, and dipole moments of the ground and some of the excited states, are estimated and compared with the existing data.

2. Computational details

The average relativistic effective potentials (AREP) of Hurley et al. [30] are employed to replace 18 core electrons of the Ge atom and the remaining $3d^{10}4s^24p^2$ electrons are placed in the valence shell for the CI calculations. Similarly, the $1s^22s^22p^6$ core electrons of Si are replaced by the AREP of Pacios and Christiansen [31], while the valence electrons are kept in the active CI space. The primitive Gaussian basis functions (3s3p4d) of Ge are taken from Hurley et al. [30]. These are augmented with two d polarization functions ($\zeta_d = 0.424$ and 0.15 a_0^{-2}) and one 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. Therefore, the final AO basis sets for Ge become (3s3p6d1f/3s3d3p5d1f). The (4s4p) primitive Gaussian functions of Pacios and Christiansen [31] for the Si atom are also augmented with many diffuse and polarization functions. Three s functions ($\zeta_s = 0.04525$, 0.02715, and 0.0163 a_0^{-2}), two p functions ($\zeta_p = 0.06911$ and 0.02499 a_0^{-2}), five d functions ($\zeta_d = 4.04168$, 1.46155, 0.52852, 0.19112, and 0.06911 a_0^{-2}), and two f functions ($\zeta_f = 0.19112$ and 0.06911 a_0^{-2}) are added from Matos et al. [32]. However, 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. So, the resulting basis set for Si used in the present CI calculations is (7s6p5d2f/7s6p4d1f). Using the Gaussian basis functions and the AREP mentioned above, self-consistent-field (SCF) calculations are performed for the $^3\Sigma^-$ state with 18 active electrons at different internuclear distances ranging from 3.0 to 20.0 a_0. The calculations have been carried out in the C_{2v} subgroup to take advantage of the simplicity of the Abelian group's direct product relationship. We have kept Ge at the origin and Si along the +z axis. The symmetry adapted optimized SCF-MOs are subsequently used as a one electron basis for the generation of configurations in the CI calculations.

The MRDCI codes of Buenker and co-workers [33–38] are employed for the CI calculations. The calculations of Λ-S states are carried out by incorporating all the relativistic effects except the spin–orbit term through AREP. Preliminary calculations show that the $3d^{10}$ electrons of Ge are not involved in the bonding of the low-lying electronic states of GeSi. Therefore, we have kept the 10 3d-electrons frozen in the CI steps and only eight electrons remain in the active space. This reduces the number of required configurations considerably. For the electronic states of a given spatial and spin symmetry, a set of reference configurations is chosen for excitations. All possible single and double excitations are allowed for each of these reference configurations. We have optimized the lowest eight roots for the triplets, five roots for the singlets, and three roots for the quintets of GeSi. A maximum number of about 10 million configurations is generated. However, the configuration selection method has been used to reduce the size of the secular equations. In the present calculations, we have employed a configuration selection threshold of 3.5 μ hartree so that the largest dimension of the selected CI space remains within 50 000. The sum of the squares of the coefficients of the reference configurations remains above 0.90. The energy extrapolation technique has been used to estimate energies at zero threshold. The effect of higher order excitations from these reference configurations is partly adjusted by the multireference analogue of the Davidson correction [39,40]. Spectroscopic and transition properties of the Λ-S states of GeSi are determined from the estimated full CI energies and wave functions.

In addition to the estimation of the spectroscopic parameters of the Λ-S states, the effect of the spin–orbit coupling has also been studied in the next step by employing the spin–orbit operators compatible with AREP of Ge and Si. In general, the spin-independent MRDCI wave functions are multiplied with appropriate spin functions, which are transformed according to the irreducible representation of C_{2v}. After the spin–orbit coupling, the Ω states belong to the A_1, A_2, and B_1/B_2 representations of C_{2v}^2 double group. The estimated full CI energies in the Λ-S CI calculations occupy the diagonals of the Hamiltonian matrix, while the off diagonal elements are calculated from the AREP based spin–orbit operators and Λ-S CI wave functions. Energies and wave functions of the spin–orbit states are obtained from the diagonalization of these spin–orbit blocks. Subsequently, spectroscopic properties of the low-lying Ω states are determined.

Potential energy curves of both spin-independent and spin-included states of GeSi are fitted to polynomials and the nuclear Schrödinger equations are solved numerically to compute the vibrational energies and wave functions [41]. Transition dipole moments are then calculated for the pair of vibrational functions involved in a particular transition. Einstein spontaneous emission coefficients and transition probabilities are calculated for dipole allowed and spin-forbidden transitions [42–44]. The radiative lifetimes of the excited states at different vibrational levels are estimated from the transition probability data.

3. Results and discussion

3.1. Potential energy curves and spectroscopic constants of Λ-S states

Atomic energy levels [45] of Ge and Si show that the ground states of both the atoms are in the ^3P_g symmetry. Eighteen Λ-S states of singlet, triplet, and quintet spin multiplicities correlate with the ground states of Ge and Si. The second and third dissociation limits of GeSi are nearly degenerate. Both the limits correlate with the excited triplets of Σ^+, $\Sigma^-(2)$, $\Pi(3)$, $\Delta(2)$, and Φ symmetries. The relative energy difference between these two limits is about 125 cm^{-1}, while the value calculated from the CI energies