

Electronic structures of linear germane–silane copolymer radical anions $[\text{Me}(\text{SiMe}_2)_n(\text{GeMe}_2)_n\text{Me}]^-$ ($n = 3-7$) in ground and low-lying excited states. A theoretical study

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Abstract

The electronic structures for the ground and low-lying excited states of linear germane–silane (Ge/Si) copolymer radical anions have been determined by means of the semi-empirical PM3-CI method. The permethylgermane–silane radical anion $[\text{Me}(\text{SiMe}_2)_n(\text{GeMe}_2)_n\text{Me}]^-$ ($n = 3-7$) was chosen as a model compound of Ge/Si copolymer radical anion. In all Ge/Si copolymers, an unpaired electron is only localized on the Ge-site, although a Si atom binding to Ge atom has a slight spin density. The spin orbital is σ^* type composed of 4p orbitals in Ge atoms. The CI calculation predicted that the radical anions have an absorption band in IR region. The excitation energy for IR band is slightly blue-shifted as a function of number of chain atoms and the oscillator strength is largely increased. The band structure for the radical anions is discussed on the basis of theoretical results. © 1997 Elsevier Science S.A.

1. Introduction

Polysilanes and polygermanes have recently received considerable attention owing to their promising physical properties such as semiconductivity, photoconductivity, photoluminescence and third-order nonlinear effects [1–12]. These properties originate from the characteristic electronic structure. In addition, the oligo- and polysilanes and germanes easily form the ionic species by one-electron oxidation and reduction [13] (i.e., radical cations and anions, respectively).

In our previous papers [14,15], the electronic structures of the linear polysilane radical cations $[\text{Si}_n(\text{Me})_{2n+2}]^+$ (where $n = 4-18$) and anions $[\text{Si}_n(\text{Me})_{2n+2}]^-$ (where $n = 6-20$) for the ground and low-lying excited states have been determined by means of both MM2-MD dynamics and PM3-CI methods. The calculations for the cations suggested that (1) an unpaired electron is widely delocalized along the Si main chain and slightly diffuses to CH_3 side chain, (2) the spin orbital is Si–Si σ -bonding type at the ground state, and (3) the wave functions for the ground and first excited states are composed of single and double Slater

determinants, respectively. For the linear polysilane radical anions, it was suggested that (1) an unpaired electron is delocalized in Si main chain as well as the cation, and (2) the excess electron is occupied in a in-plane π^* orbital corresponding to LUMO of the neutral polysilane.

Recently, electroreductive synthesis of the linear copolymers, composed of silicon and germanium in its main chain, have been possible [16], and several properties of the copolymers have been investigated experimentally. Although the neutral state of the copolymers have been investigated extensively, the electronic states of the ionic species of the copolymers, which play an important role in one-dimensional conductor, are scarcely known. Especially, there is no detailed theoretical work on the ionic species of Ge/Si copolymer. Hence, theoretical characterization of the oligosilane/germane radical ions may provide useful information of mechanism as a one-dimensional conductor.

In the present paper, we have extended the study to the linear oligosilane/germane radical anions $[\text{Me}(\text{SiMe}_2)_n(\text{GeMe}_2)_n\text{Me}]^-$ ($n = 3-7$). The electronic states and absorption spectra are predicted by semi-empirical PM3-CI calculations. The band structure will be discussed on the basis of the theoretical results. For

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comparison, the asymmetric copolymer $[\text{Me}(\text{SiMe}_2)_6 - (\text{GeMe}_2)_m\text{Me}]^-$ ($n = 6, m = 1-4$) was also studied.

2. Method of the calculations

In our previous papers [14,15], we have calculated the electronic states of polysilane radical ions by means of the PM3-MO and CI calculations [17,18]. The PM3-MO calculations gave reasonable electronic and geometrical structures of the linear polysilane radical anions and cations. In addition, the results derived from

the calculations were in good agreement with the experiments [11,12]. Therefore, we used the same manner throughout the present study. The oligomer (copolymer) radical anion, composed of both Si and Ge sites, $[\text{Me}(\text{SiMe}_2)_n - (\text{GeMe}_2)_n\text{Me}]^-$ ($n = 3-7$), was chosen as a model for the germane and silane copolymer.

The copolymer is expected to have several conformations at room temperature in condensed phase, so that initial geometry of the copolymer was chosen through the following procedure.

(1) Structure of the neutral permethyl copolymer $[\text{Me}(\text{SiMe}_2)_n(\text{GeMe}_2)_n\text{Me}]$ ($n = 3-7$) is generated by

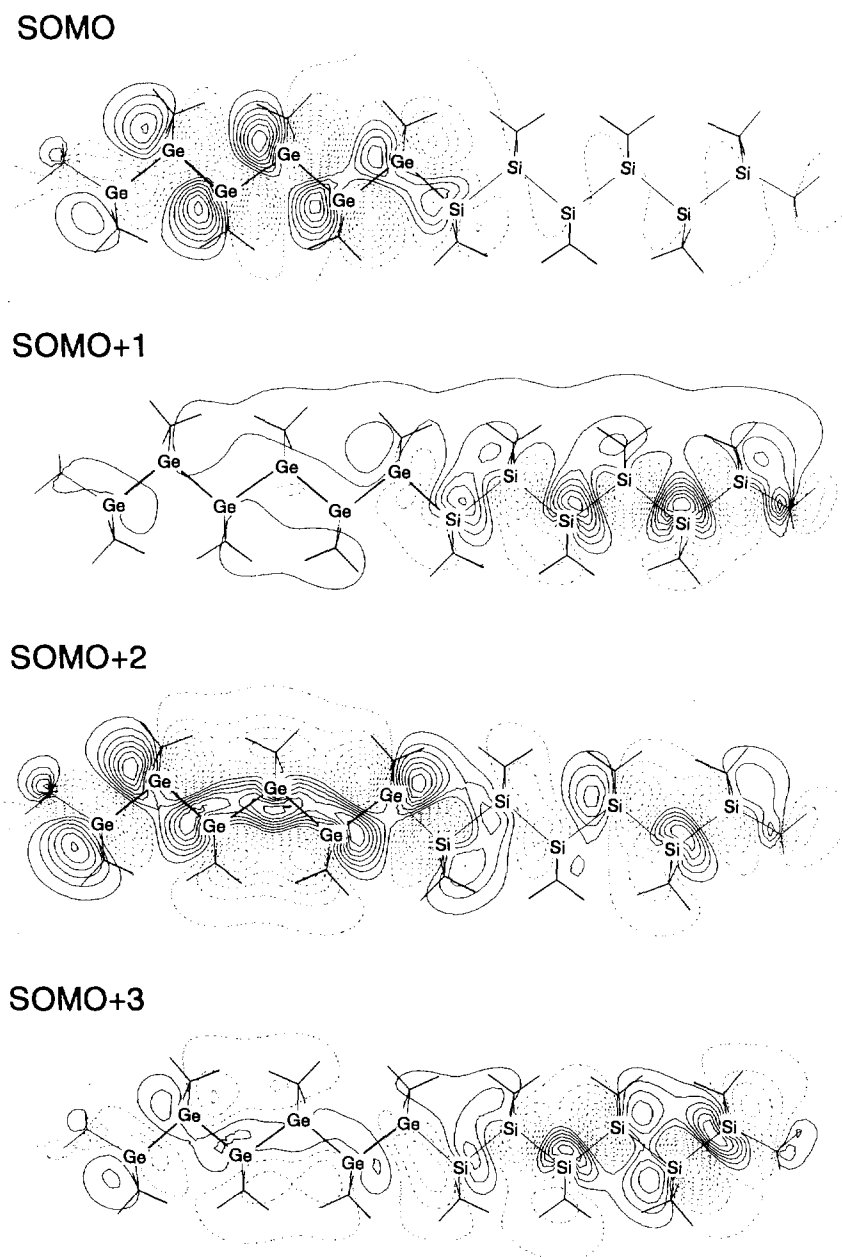


Fig. 1. Contour plots of molecular orbitals for $\text{SOMO} + i$ ($i = 0-3$) of the silane-germane copolymer radical anion ($n = 6$) calculated by the PM3-MO method.

the MM2 method. All *trans* forms are assumed as an initial geometry.

(2) In order to obtain more relevant structure at room temperature, molecular dynamic (MD) calculation with the MM2 potential function is performed up to 3.0 ps from the MM2 optimized structure (constant temperature: 300 K).

(3) After the MD calculation, the final structure is further optimized by the PM3 molecular orbital (MO) calculation with the energy gradient method. One can obtain the geometry of the neutral copolymer $[\text{Me}(\text{SiMe}_2)_n(\text{GeMe}_2)_n\text{Me}]$ ($n = 3-7$) at the PM3-MO level.

(4) The geometry of the copolymer radical anion $[\text{Me}(\text{SiMe}_2)_n(\text{GeMe}_2)_n\text{Me}]^-$ ($n = 3-7$) is fully optimized from the geometry of the neutral molecule obtained by the PM3 optimization.

The electronic states of the radical anions were calculated by means of the PM3-CI method with the PM3-MO optimized geometries thus obtained.¹ Three occupied and three virtual orbitals with five electrons are considered as active space in the CI calculation. A copolymer, which is randomly bonded by both Si and Ge atoms, is not considered in the present study.

3. Results

3.1. Structures

Each structure of germane–silane (Ge/Si) copolymers and its radical anions are geometrically optimized by the PM3-MO method. We assumed the linear form of the copolymer as initial structure. The PM3-MO calculation for the neutral structure shows that the geometry retains the regular linear form as a most stable structure. The PM3 optimization for the radical anion gives the regular linear form as the most stable form as well as that of the neutral state.

In this section, the structure of the Ge/Si copolymer will be explained by using the copolymer with $n = 6$ as an example. The averaged distances of Ge–Ge and Si–Si bonds for the anionic state is slightly shorter than that of neutral state, although the difference is negligibly small. For example, in case of $n = 6$, the averaged Ge–Ge, Ge–Si, and Si–Si distances are 2.411 Å, 2.427 Å, and 2.421 Å for anionic system, and 2.411 Å, 2.427 Å and 2.422 Å for the neutral system. The distances between terminal Ge–Si atoms are calculated to 20.57 Å for the neutral and 20.60 Å for the anionic states. These results suggest that the molecular structure of the Ge/Si copolymer is hardly changed by accepting an

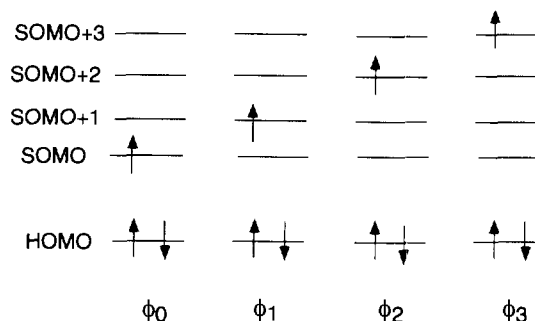


Fig. 2. Schematic representation of important configuration state functions (CSFs) of the linear copolymer radical anion.

excess electron. This is an important property as one-dimensional semi-conductor in polysilane.

3.2. Electronic states

3.2.1. Spin orbital at the ground state

The electronic states of the Ge/Si copolymer radical anions are calculated with each optimized structure. In this section, we explain the electronic states by using the results for the radical anion with $n = 6$. The spin orbital (singly occupied molecular orbital: SOMO) having an excess electron is illustrated in Fig. 1 as contour map. As can be seen clearly, the excess electron is almost localized on Ge-site, although the spin contaminates slightly to Si atom connecting to Ge atom. The spin orbital is $\sigma^*(\text{Ge-Ge})$ type composed of 4p orbitals of Ge atoms. This orbital corresponds to the lowest unoccupied molecular orbital (LUMO) of the neutral copolymer. The spin orbital indicates that the excess electron is distributed along the main chain and that all Ge atoms have positive spin densities. On the other hand, the methyl group has negative spin densities.

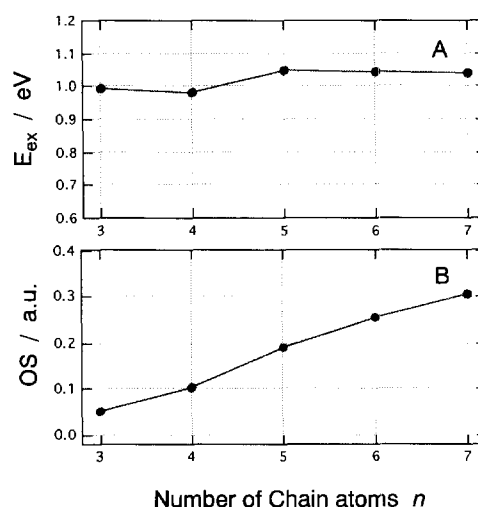


Fig. 3. Excitation energies (A) and oscillator strengths (B) plotted as a function of number of chain atoms n . The values are calculated by the PM3-CI method.

¹ The Z-matrices of all optimized structures are available upon request. E-mail address: hiroto@pc.cfa.hokudai.ac.jp.

Table 1

CI coefficients (c_0 , c_1 , c_2 , and c_3) of configuration state functions (CSFs) for the ground (ϕ_0) and first excited states (ϕ_1 , ϕ_2 and ϕ_3) of the linear Ge/Si copolymer radical cations.

| n | First excited state | | | |
|-----|---------------------|----------|----------|----------|
| | ϕ_0 | ϕ_1 | ϕ_2 | ϕ_3 |
| 3 | 0.993 | -0.235 | -0.849 | -0.380 |
| 4 | 0.993 | 0.260 | -0.865 | -0.203 |
| 5 | 0.993 | -0.232 | -0.872 | 0.345 |
| 6 | 0.994 | -0.210 | -0.898 | 0.315 |
| 7 | 0.993 | 0.183 | -0.915 | 0.284 |

3.2.2. CI calculations

Wave functions for the ground and first excited states are calculated at the PM3-CI levels. The important configuration state functions (CSFs) are illustrated in Fig. 2. The notation of ϕ_i in Fig. 2 means i th CSF generated from Hartree–Fock molecular orbitals. The ϕ_i corresponds to a configuration where an excess electron is located in i th singly occupied molecular orbital (SOMO + i). For example, ϕ_0 means that the excess electron occupies in SOMO ($i = 0$), and ϕ_1 is in (SOMO + 1) orbital. In the present study, four configurations ϕ_0 , ϕ_1 , ϕ_2 , and ϕ_3 become important ones as will be seen in a later section.

The CI calculations show that the main configuration for the ground state is composed of only ϕ_0 . This means that the ground state is mainly expressed by single determinant of SOMO (ϕ_0) at the ground state. The CI coefficient of ϕ_0 has an almost constant value up to $n = 7$. In contrast, the first excited state is composed of three CSFs (ϕ_1 , ϕ_2 and ϕ_3), although the main configuration (> 80%) is ϕ_2 . The CI coefficients of three CSFs are strongly affected by number of chain atoms: the weight of ϕ_2 is larger at longer chain length. This implies that configuration of ϕ_2 becomes a main configuration at infinity of chain length.

The first excitation energy (E_{ex}) is listed in Table 1. The excitation energy is slightly blue-shifted as a function of n , although the shift is very small. In contrast, the oscillator strengths (OSs) for the first excitation largely increase. The values of OSs are calculated at 0.05 a.u. for $n = 3$ and 0.31 a.u. for $n = 7$ (Fig. 3). The reason why the OS increases with increasing n will be discussed in Section 4.

4. Discussion

On the basis of the present calculations, the band structure of Ge/Si copolymer system is constructed as illustrated in Fig. 4. The highest energy level of valence band in Ge site is slightly lower than that of the Si-site. In contrast, the conduction band is delocalized on both Ge- and Si-sites. These features are derived from the

orbital picture near HOMO level, such as contour maps (Fig. 1). An energy level of anion state, which is a discrete level, is slightly lower than that of bottom of conduction band. It should be noted that the anion state is mainly localized on the Ge-site (a real line below the conduction band) and slightly contaminates to the Si-site, as illustrated by a dashed line.

The CI calculation predicted that first electronic transition can be observed as an IR band. Although the excitation energy for the IR band is hardly changed by number of chain atoms up to $n = 7$, its intensity is strongly affected. This feature is reasonably explained by the following simple consideration. Wave function of the copolymer is expressed by

$$\psi = \sum_i c_i \phi_i$$

The CI calculations suggest that the ground and first excited state wave functions are approximately given by

$$\psi_0 \cong c_0 \phi_0 \text{ and } \psi_1 \cong c_2^* \phi_2^* + c_3^* \phi_3^*$$

respectively. The CI coefficients for the excited state indicates $c_3^* \ll c_2^*$, so that the transition moment (μ) for the IR band is approximately expressed by

$$\mu \cong c_0 c_2^* \langle \phi_0 | \mu | \phi_2^* \rangle.$$

In addition, coefficient c_0 is almost constant up to $n = 7$, so that the transition moment is simply given by

$$\mu \cong \text{constant} \times c_2^*$$

This means that the transition moment for the IR band is linearly proportional to a coefficient c_2^* . As shown in Table 1, oscillator strength is actually proportional to the coefficient c_2^* . Therefore, the intensity of the IR band increases with increasing number of chain atom.

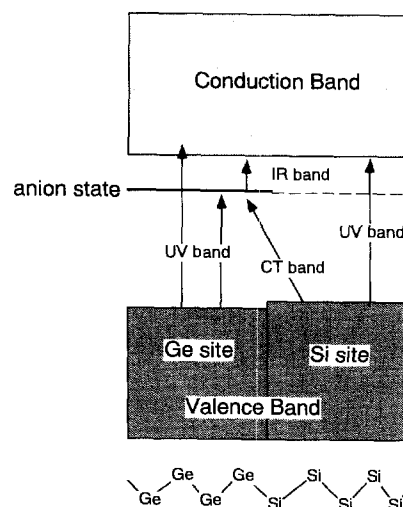


Fig. 4. Schematic representation of the band structures for silane-germane copolymer radical anions.

The CI calculations also indicate that the UV bands can be assigned to a transition from the valence band to the conduction band. In addition, it is predicted that a charge transfer band from the valence band in the Si-site to the anionic state appears at UV/VIS region, although the intensity of the absorption band is weaker than that of IR band.

In order to check the electronic states obtained by PM3 calculations, ab initio MO calculation was preliminary carried out for $[\text{H}(\text{SiH}_2)_3-(\text{GeH}_2)\text{H}]^-$ at the HF/3-21G level. The calculation of the spin densities indicated that the unpaired electron is about 80% localized on the Ge-site, which is in good agreement with that of PM3 method. This implies that PM3 calculation is enough to discuss qualitatively the electronic state of the copolymers.

In the present calculation, we considered only symmetric Ge/Si copolymer $[\text{Me}(\text{SiMe}_2)_n-(\text{GeMe}_2)_m\text{Me}]^-$ ($n = m$). The calculation indicates that the excess electron is mainly localized in Ge-site. This is due to the fact that SOMO of Ge-site is much lower than that of Si-site, that is, the electron affinity in Ge-site is larger than that of Si-site. The calculations of electronic states for asymmetric Ge/Si copolymers $[\text{Me}(\text{SiMe}_2)_n-(\text{GeMe}_2)_m\text{Me}]^-$ ($n \neq m$) and random copolymers are now in progress [19].

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