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Structural, electronic and vibrational properties of Ge_xC_y $(x+y=2–5)$ nanoclusters: A B3LYP-DFT study

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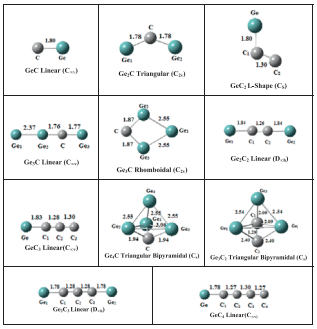
HIGHLIGHTS

- The stability, structural and electronic properties of Ge_xC_y clusters.
- Vibrational and optical properties are investigated only for the most stable structures.
- The most stable structures are those which contain the maximum number of carbon atoms.
- The nanoclusters containing even (odd) number of carbon atoms have large(small) HOMO–LUMO gap.
- Our calculated frequencies are, in general, 0.5–5% higher than the experimental data.

GRAPHICAL ABSTRACT

Optimized most stable geometries of Ge_xC_y $(x+y=2–5)$ nanoclusters.



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ABSTRACT

An *ab-initio* study of the stability, structural and electronic properties has been made for 84 germanium carbide nanoclusters, Ge_xC_y $(x+y=2–5)$. The configuration possessing the maximum value of final binding energy (FBE), among the various configurations corresponding to a fixed $x+y=n$ value, is named as the most stable structure. The vibrational and optical properties have been investigated only for the most stable structures. A B3LYP-DFT/6-311G(3df) method has been employed to optimize fully the geometries of the nanoclusters. The binding energies (BE), highest-occupied and lowest-unoccupied molecular orbital (HOMO–LUMO) gaps have been obtained for all the clusters and the bond lengths have been reported for the most stable clusters. We have considered the zero point energy (ZPE) corrections. The adiabatic and vertical ionization potentials (IPs) and electron affinities (EAs), charge on atoms, dipole moments, vibrational frequencies, infrared intensities (IR Int.), relative infrared intensities (Rel. IR Int.) and Raman scattering activities have also been investigated for the most stable structures. The configurations containing the carbon atoms in majority are seen to be the most stable structures. The strong C–C bond has important role in stabilizing the clusters. For the clusters containing one germanium atom and all the other as carbon atoms, the BE increases monotonically with the number of the carbon atoms. The HOMO–LUMO gap, IPs and EAs fluctuates with increase in the number of atoms. The nanoclusters containing even number of carbon atoms have large HOMO–LUMO gaps and IPs, whereas the nanoclusters containing even number of carbon atoms have small EAs. In general, the adiabatic IP (EA) is smaller (greater) than the vertical IP (EA). The optical absorption spectrum or electron energy loss

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spectrum (EELS) is unique for every cluster, and may be used to characterize a specific cluster. All the predicted physical quantities are in good agreement with the experimental data wherever available. The growth of these most stable structures should be possible in the experiments.

1. Introduction

The field of atomic nanoclusters, which form a link between molecules and solids, is an active area of research over many years due to its fundamental scientific and technological importance. In clusters, the high surface area to volume ratio is quite high as compared to bulk [1,2]. The sizes of the electronic devices have been reduced because of this advancement. A fundamental issue is to understand how the atomic and electronic structures and properties of the clusters change with its aggregation size increasing from single atom to bulk materials.

In recent years, the group IV–IV materials have held a growing interest for both experimental and theoretical researchers, mainly due to their extraordinary electronic structures and potential usages in optoelectronics and semiconductor applications and their possible existence in interstellar space [3–12]. Germanium and carbon are also important components of nanomaterials. Over last several years, Germanium and carbon clusters have been the subject of intensive studies. Germanium carbide is a wide-band gap semiconductor and is an attractive material from a technological point due to its high potential in electrical and high temperature mechanical devices. It has been suggested that Ge–C may have particularly unique optoelectronic properties for application such as high band gap semiconductor on Si.

Chemical precursors were used to grow crystalline GeC materials with unusual morphologies that depend on the molecular design of the precursor and the C concentration [13]. Such systems may be useful for the band gap engineering, as the gaps may be controlled by the C content [14]. These materials draw further attention due to potential applications of nanostructures in nanowires and nanorods.

The structural and electronic properties of GeC was first reported by Sankey et al. [15]. Later energies and structural properties of the GeC molecule have been determined by Sefyani et al. [16] via *ab initio* multireference configuration interaction calculations.

Although there are thousands of studies of carbon–germanium and silicon–germanium molecules in both solid and gas phases, there are few mass spectrometric measurements of GeC and on spectroscopic and one infrared study of GeSi. The first mass

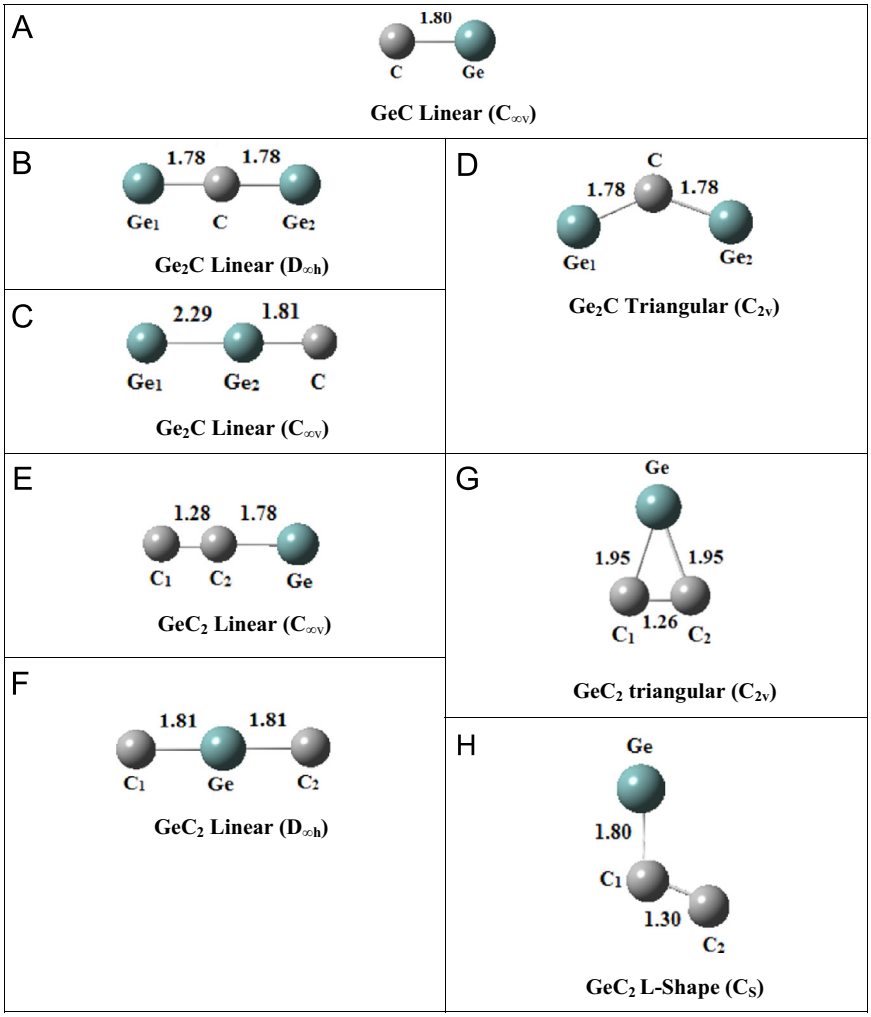

Fig. 1. Optimized structures of Ge_xC_y ($x+y=2$–3) nanoclusters. The bond lengths are in Å.