Germanium Dicarbide: Evidence for a T-shaped Ground State Structure

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Since the late 1950s:
Discussion about the structure of GeC₂

Isovalent to SiC₂ ($C_{2V}$ structure\(^{1}\))

Metal Dicarbides MC₂ are detected in space (e.g. C₂O² and SiC₂³)

Carbon-rich Group 14 materials: Attractive for nanoelectronics and material science

GeC$_2$ – A vivid example

- Since the late 1950s:
  - Discussion about the structure of GeC$_2$
- Isovalent to SiC$_2$ ($C_{2v}$ structure$^1$)
- Metal Dicarbides MC$_2$ are detected in space (e.g. C$_2$O$_2$ and SiC$_2^3$)
- Carbon-rich Group 14 materials: Attractive for nanoelectronics and material science

GeC$_2$ – Structural debate

linear

$\text{Ge} \quad \text{C} \quad \text{C}$
Mass Spectrometric Study of Inter-Group IVB Molecules*

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(Received August 8, 1958)

The systems germanium-graphite and germanium-silicon-carbon have been studied. Several gaseous molecules containing Ge, Si, and/or C were observed and their dissociation energies determined from measured partial pressures. A general picture of the dissociation energies of di-, tri-, and tetraatomic intergroup IVB molecules is deduced from these measurements.

Incidental to this study the vapor pressure of pure Si was determined; the result confirms the heat of sublimation obtained previously.

Structure and stability of GeₙCₘ₋ₙ clusters

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Received 21 January 2003; revised 3 March 2003; accepted 6 March 2003

Abstract
Density functional theory method has been used to predict the structural and energetic properties of GeₙCₘ₋ₙ (n = 1, m = 3–14; n = 2, m = 4–15) isomers. The optimized stable structures have been found to be linear(chain) for all GeₙCₘ₋ₙ (n = 1, m = 3–9; n = 2, m = 4–10) clusters and planar(ring) for all GeₙCₘ₋ₙ (n = 1, m = 10–14; n = 2, m = 11–15) isomers. It has been also found that the GeₙCₘ₋ₙ (n = 1, m = 3–14; n = 2, m = 4–15) clusters with odd m are more stable than those with even m.

Keywords: GeₙCₘ₋ₙ clusters; Stability; Dipole moment; Density functional theory; B3LYP
GeC$_2$ – Structural debate

T-shaped
The Knudsen effusion mass spectrometric method was used in measuring the partial pressures of GeC₂, Ge₂C, Ge₃C, and Ge₄C above liquid germanium which was contained in a graphite Knudsen cell. These partial pressures have been combined with calculated thermal functions to determine the atomization enthalpies, ΔHₘₐₓ (in kJ mol⁻¹): 1197 ± 10 (GeC₂); 902 ± 12 (Ge₂C); 1247 ± 22 (Ge₃C); and 1535 ± 25 (Ge₄C). The enthalpies of formation, ΔHₚₑᵢₚ (in kJ mol⁻¹) are 597 ± 10 (GeC₂); 555 ± 12 (Ge₂C); 579 ± 22 (Ge₃C); and 630 ± 25 (Ge₄C).
GeC$_2$ – Structural debate

L-shaped
GeC$_2$ – Structural debate

L-shaped

Structure and bonding in third-row main group dicarbides C$_2$X (X=K–Br)

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Thermodynamic properties of germanium/carbon microclusters

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(Received 9 September 2005; accepted 20 October 2005; published online 22 December 2005)
An L-shaped equilibrium geometry for germanium dicarbide (GeC$_2$)?
Interesting effects of zero-point vibration, scalar relativity, and core–valence correlation

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(Received 11 July 2002; accepted 12 September 2002)

The ground state potential energy surface of the GeC$_2$ molecule has been investigated at highly correlated coupled cluster levels of theory. Large basis sets including diffuse functions and functions to describe core correlation effects were employed in order to predict the true equilibrium geometry for GeC$_2$. Like the much-studied valence isoelectronic SiC$_2$, the linear (\(^1\Sigma^+\)), L-shaped (\(^1\Lambda'\)), and T-shaped structures (\(^1\Lambda_1\)) must be investigated. The L-shaped C$_5$ geometry is found to have real harmonic vibrational frequencies along every internal coordinate, and the linear stationary point has an imaginary vibrational frequency along the bending mode at every level of theory employed. The T-shaped geometry is found to have an imaginary vibrational frequency along the asymmetric stretching mode. At the coupled cluster with single and double excitations and perturbative triple excitations [CCSD(T)]/correlation consistent polarized valence quadrupole-\(\zeta\) (cc-pVQZ) level, the nonrelativistic classical relative energies of the T-shaped and linear structures with respect to the L-shaped minimum are 0.1 and 2.8 kcal/mol, respectively. Including zero-point vibrational energy, scalar relativistic, and core-valence corrections, the T-L energy separation is shifted to 0.4 kcal/mol and the relative energy between the L-shaped and linear structures is still 2.8 kcal/mol. All nonrelativistic and relativistic computations predict that the L-shaped (\(^1\Lambda'\)) structure is most favored for the ground state. The linear structure is predicted to be a transition state, as the case of SiC$_2$. © 2002 American Institute of Physics. [DOI: 10.1063/1.1518966]
GeC$_2$ — Structural debate

T-shaped

L-shaped

L-shaped

L-shaped

Ge

C

C

Ge

C

C

2.8 kcal/mol

0.4 kcal/mol

Linear
Chirped-Pulse Spectrometer

1. Pulsed nozzle
2. Supersonic expansion
3. Fixed mirror
4. Movable mirror
5. Microwave emitter/receiver
6. Microwave absorbers
7. Horn antenna
8. Horn antenna

t ≈ 17 hr
\[ J'_{Ka'Kc'} - J''_{Ka''Kc''} = 1_{01} - 0_{00} \]

- \( \text{\(^{74}\text{GeC}_2\)} \)
  - \( n = 36\% \)

- \( \text{\(^{72}\text{GeC}_2\)} \)
  - \( n = 28\% \)

- \( \text{\(^{76}\text{GeC}_2\)} \)
  - \( n = 8\% \)

- \( \text{\(^{73}\text{GeC}_2\)} \)
  - \( n = 8\% \)

- \( \text{\(^{70}\text{GeC}_2\)} \)
  - \( n = 21\% \)
Wealth of Isotopologues
Wealth of Isotopologues

\[
\begin{align*}
\text{76}^{\text{13}}\text{Ge} & \quad \text{CC} \\
\text{74}^{\text{13}}\text{Ge} & \quad \text{CC} \\
\text{72}^{\text{13}}\text{Ge} & \quad \text{CC} \\
\text{70}^{\text{13}}\text{Ge} & \quad \text{CC}
\end{align*}
\]

Frequency (MHz)
W-Band spectrometer

- Commercial chirped spectrometer
- 75-115 GHz
W-Band measurement

Frequency (GHz)
## Rotational parameters

<table>
<thead>
<tr>
<th></th>
<th>Constant</th>
<th>$^{12}$C$_2$</th>
<th>$^{12}$C$^{13}$C</th>
<th>$^{13}$C$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{70}$Ge</td>
<td>$A_0$</td>
<td>[53431.4]</td>
<td>51397.0(201)</td>
<td>49297.4(221)</td>
</tr>
<tr>
<td></td>
<td>$(B_0 + C_0)/2$</td>
<td>7745.5872(50)</td>
<td>7512.07635(120)</td>
<td>7294.79366(198)</td>
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<tr>
<td></td>
<td>$(B_0 - C_0)/4$</td>
<td>317.74(39)</td>
<td>306.80032(85)</td>
<td>301.07628(85)</td>
</tr>
<tr>
<td>$^{72}$Ge</td>
<td>$A_0$</td>
<td>[53431.4]</td>
<td>51381.8(207)</td>
<td>49309.0(228)</td>
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<tr>
<td></td>
<td>$(B_0 + C_0)/2$</td>
<td>7694.1462(52)</td>
<td>7460.67187(120)</td>
<td>7243.44571(198)</td>
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<tr>
<td></td>
<td>$(B_0 - C_0)/4$</td>
<td>313.80(40)</td>
<td>302.63221(85)</td>
<td>296.87040(85)</td>
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<tr>
<td>$^{73}$Ge</td>
<td>$A_0$</td>
<td>[53431.4]</td>
<td>51377.9(109)</td>
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<tr>
<td></td>
<td>$(B_0 + C_0)/2$</td>
<td>7669.41276(58)</td>
<td>7435.95145(144)</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>$(B_0 - C_0)/4$</td>
<td>311.744(60)</td>
<td>300.6374(48)</td>
<td>–</td>
</tr>
<tr>
<td>$^{74}$Ge</td>
<td>$A_0$</td>
<td>[53431.4]</td>
<td>51382.3(213)</td>
<td>49308.4(235)</td>
</tr>
<tr>
<td></td>
<td>$(B_0 + C_0)/2$</td>
<td>7645.4226(53)</td>
<td>7411.97649(120)</td>
<td>7194.80702(198)</td>
</tr>
<tr>
<td></td>
<td>$(B_0 - C_0)/4$</td>
<td>309.72(42)</td>
<td>298.70926(85)</td>
<td>292.91178(85)</td>
</tr>
<tr>
<td>$^{76}$Ge</td>
<td>$A_0$</td>
<td>[53431.4]</td>
<td>51343.6(90)</td>
<td>[49308.6]</td>
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<tr>
<td></td>
<td>$(B_0 + C_0)/2$</td>
<td>7599.2042(55)</td>
<td>7365.78453(95)</td>
<td>7148.66602(112)</td>
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<tr>
<td></td>
<td>$(B_0 - C_0)/4$</td>
<td>305.93(44)</td>
<td>295.01088(88)</td>
<td>289.18212(88)</td>
</tr>
</tbody>
</table>
Structural parameters

CCSD(T)/cc-pwCVQZ - level

14.74 kJ/mol

0.02 kJ/mol
### Structural parameters

**CCSD(T)/cc-pwCVQZ - level**

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<tr>
<td>$r_{\text{Ge-C}}$/Å</td>
<td>1.952(1)</td>
<td>1.9296</td>
<td>1.8184</td>
<td>1.7717</td>
</tr>
<tr>
<td>$r_{\text{Ge-C}}$/Å</td>
<td>1.294</td>
<td>1.2750</td>
<td>1.2810</td>
<td>1.2836</td>
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<tr>
<td>Apex angle /°</td>
<td>38.7(2)</td>
<td>38.58</td>
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CCSD(T)/cc-pwCVQZ - level

- 0.02 kJ/mol
- 14.74 kJ/mol
Acknowledgments

Thank you for your attention!

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+ P. Antonucci

Justin Neill and Matt Muckle