Theoretical and Computational Studies of Interstellar C_{2n}H and SiC_{2m+1}H

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Theoretical and Computational Studies of Interstellar \( C_{2n}H \) and \( SiC_{2m+1}H \)

Ryan Fortenberry

Virginia Tech

Invent the Future
Introduction

Astrobiology

Titan

Pillars of Creation

Interstellar Spectra

DIBs

Computational Tools
• RHF, ROHF, UHF, and Brueckner CCSD and CCSD(T).
• Analytic energy gradients for CCSD and CCSD(T).
• Excitation energies: CIS(D), EOM-CCSD, and CC3.
• Coupled cluster linear response CC2 and CCSD.
• Multireference CCSD and CCSD(T).
• Determinant-based CI methods, including full-CI.
• Integral direct SCF, MP2, and MP2-R12.
• Diagonal Born-Oppenheimer corrections.
• Arbitrarily high angular momentum in basis sets.
• Written in the C and C++ programming languages.
• Open source and available at www.psicode.org.

The PSI3 Quantum Chemistry Suite


*J. Comp. Chem. 28, 1610-1617 (2007).*
Carriers must contain H, C, N, and O where C is the dominant element. Si, Al, P, S, Cl, Li, F, and others may be present but not as abundant.

Proposed Carriers include:

- Atomic Species
- Dust Grains
- Fullerenes
- Polycyclic Aromatic Hydrocarbons (PAHs)
- Linear Chains
  - Carbon only chains, $C_n$.
  - Monohydrogen polyacetylenes, $C_nH$.
  - Cyanopolyacetylenes, $NC_nH$.

• Are the $\cdot C_{2n}H$ and $\cdot SiC_{2m+1}H$ family of molecules carriers of any of the DIBs?

• What is the electronic behavior of these molecules?

• What is the ground state ($^2\Sigma$ or $^2\Pi$)?

• What do their electronic spectra look like?
The optimal geometries and energies for the systems of interest were calculated using cc-pVDZ and cc-pVTZ basis sets.

The methods, references, and packages included:

- UHF-CCSD - PSI3
- UHF-CCSD(T) - PSI3 & ACES II
- ROHF-CCSD(T) - PSI3 & ACES II
- QRHF-CCSD(T) - ACES II
- EOMIP-CCSD - ACES II
\( \text{\( \cdot \)C}_{2n}\text{H} \text{ and \( \cdot \)SiC}_{2m+1}\text{H Results} \)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Ground State</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \cdot \text{C}_2\text{H} )</td>
<td>( ^2\Sigma^+ )</td>
</tr>
<tr>
<td>( \cdot \text{C}_6\text{H} )</td>
<td>( ^2\Pi )</td>
</tr>
<tr>
<td>( \cdot \text{SiCH} )</td>
<td>( ^2\Pi )</td>
</tr>
<tr>
<td>( \cdot \text{SiC}_3\text{H} )</td>
<td>( ^2\Pi )</td>
</tr>
<tr>
<td>( \cdot \text{SiC}_5\text{H} )</td>
<td>( ^2\Pi )</td>
</tr>
</tbody>
</table>

Every basis set, method, and reference combination used predicted the same ground state within the set of calculations for each individual molecule.
### C₄H Current Results

#### cc-pVDZ Results

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_{\text{Diff}}$ - kcal/mol</th>
<th>Ground State</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHF-CCSD(T)</td>
<td>2.07</td>
<td>$^2\Pi$</td>
</tr>
<tr>
<td>ROHF-CCSD(T)</td>
<td>0.75</td>
<td>$^2\Pi$</td>
</tr>
<tr>
<td>QRHF-CCSD(T)</td>
<td>3.01</td>
<td>$^2\Pi$</td>
</tr>
<tr>
<td>EOMIP-CCSD</td>
<td>1.88</td>
<td>$^2\Pi$</td>
</tr>
</tbody>
</table>

#### cc-pVTZ Results

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_{\text{Diff}}$ - kcal/mol</th>
<th>Ground State</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHF-CCSD(T)</td>
<td>0.75</td>
<td>$^2\Pi$</td>
</tr>
<tr>
<td>ROHF-CCSD(T)</td>
<td>0.44</td>
<td>$^2\Sigma^+$</td>
</tr>
<tr>
<td>QRHF-CCSD(T)</td>
<td>1.44</td>
<td>$^2\Pi$</td>
</tr>
<tr>
<td>EOMIP-CCSD</td>
<td>0.94</td>
<td>$^2\Pi$</td>
</tr>
</tbody>
</table>
Using UHF-CCSD(T)/cc-pVTZ geometries, excited states were calculated using aug-cc-pVDZ and aug-cc-pVTZ basis sets.

- CIS and TD-B3LYP were calculated using Gaussian 03.
- EOM-CCSD states were calculated with PSI3. Core electrons (1s for carbon and 1s2s2p for silicon) were held frozen in all EOM-CC calculations.
For all systems, a strong $\pi \rightarrow \pi^*$ transition was predicted, matching data from Maier and co.

This strong transition has been found to be a HOMO/LUMO transition in agreement with experiment for all but for $\cdot$SiC5H which has a HOMO-2/LUMO transition.

For each method, the spectrum is dominated by a single tall peak.

Wavelengths are too small for DIBs.
C$_2$H Spectral Results
C₄H Spectral Results
SiC$_3$H Spectral Results

![Graph showing SiC$_3$H spectral results with various absorption peaks at different wavelengths.](image)
SiC₅H Spectral Results

Graph showing absorption wavelength (nm) versus intensity. The graph includes multiple lines representing different computational methods:
- TD-B3LYP aug-cc-pVDZ
- TD-B3LYP aug-cc-pVTZ
- CIS aug-cc-pVDZ
- CIS aug-cc-pVTZ
- EOM-CCSD aug-cc-pVDZ

The y-axis represents intensity, ranging from 0.0 to 1.6, while the x-axis represents absorption wavelength, ranging from 120 to 360 nm.
The smaller systems are not carriers of the DIBs since their spectra are too far down into the UV.

However, the larger ones may still be considered.
Future Work

- Employ larger basis sets and more accurate methods to studying these and similar molecules. CC3 calculations are currently running.

- Develop our own higher accuracy methods using the PSI3 platform to calculate the excited states and generate spectra.
  - We will extend the Crawford group's CC3 method for excited states of radicals to include oscillator strengths.

- Use the techniques developed for this problem and expand to examine other potential carriers of the DIBs, like cyanopolyacetylenes, linear carbon chains, or halogenated carbon chains.
Acknowledgements

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Questions?