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UV Spectroscopy of Interstellar Radicals

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Available at: https://works.bepress.com/ryan_fortenberry/40/
The rationale for this project has development potential in three stages:

1. **Project Rationale**
   - The study of electronic spectroscopy with application to interstellar compounds has the potential to advance computational chemistry tools, interstellar electronic spectra, and astrobiology. Interstellar molecules are often of a high energy nature and are found in terrestrial conditions. Theory, by its nature, alleviates this difficulty and, thus, stands to increase its predictive power and advance the field.

2. **Computational Tools**
   - The rationale for this project has development potential in three stages:
     - **Ground State Determination**
       - The optimal geometries and energies for the four systems of interest were calculated using both CCSD(T) and CCSD(T) with the cc-pVTZ and cc-pVDZ basis sets.
       - Comparison of the energy was made for each of the four molecules between the singlet and triplet states.
       - It was found that the T1 was lower in energy for all four systems. This was in agreement with results found by Sobolewski and Adamowicz but counter to other studies found in the chemical literature for CH.

3. **Interstellar Spectra**
   - The T1 CCSD(T)/cc-pVTZ geometries were used as the optimal structures for vertical excitation energy calculations:
     - TD-B3LYP and CIS calculations with both the aug-cc-pVTZ and aug-cc-pVDZ basis sets were carried out over the potential energy surface.
     - A perturbation was used to fit the ideal spectra given by the respective codes to the data in order to simulate natural light broadening seen in laboratory experiments.

4. **UV Spectra of Interstellar Radicals**
   - Ryan Fortenberry and T. Daniel Crawford
   - Virginia Tech, Blacksburg, Virginia

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The Diffuse Interstellar Bands

Around the middle of the 20th century, a broad, highly structured spectrum containing hundreds of lines ranging from the visible to the near infrared was obtained from various sources in the ISM. It has been estimated that there are over 300 lines in the diffuse interstellar bands (DIBs) with a total strength of 1.0% of the continuum. To date, no single line has been conclusively assigned to a molecular carrier, and collaboration between theory and experiment has yet to be fruitful. The major problem with the identification of the carriers of the DIBs is the need for exceptionally precise theoretical simulations of the electronic spectra. Most quantum chemical models accurately predict spectral features of open-shell and ionic compounds incorporated in the ISM, but only very few can predict the detailed line shapes needed for the DIBs. The project here aims to develop new, high-accuracy quantum chemical methods to predict the electronic spectra of small molecules with the ultimate goal of providing unique computational tools with which astrophysicists may at last be able to determine the carriers of interstellar spectra such as the DIBs.
Conclusions & Observations

• The ground state for these linear radicals is $^2\Pi$ based on our methods.
• These radical systems all have a characteristically strong transition which is much higher than any of the other ones. This trend was seen regardless of method or basis set and was a $\pi \rightarrow \pi^*$ transition in every case.
• The most intense bands for $\cdot$C$_4$H, $\cdot$SiC$_3$H, and $\cdot$C$_6$H correspond to a HOMO($\pi$) to LUMO($\pi^*$) transition. However, for $\cdot$SiC$_5$H the most intense band corresponds to a HOMO-2($\pi$) to LUMO($\pi^*$) transition.
• Relative to EOM-CCSD, CIS overestimates the most intense transition, and TD-B3LYP underestimates it in all four systems.
• Further development of more precise codes, like CC3, for open shell systems would help to resolve the ground state debate.

References


