Optimizing Methods for Calculating the Vibrational Frequencies for the Astrochemical Species c-C₃H₂

Marisa Smedsrud & Dr. Joshua Layfield

Introduction: Starting around the mid 1800’s, stars were used as a source for spectroscopy. As a result, scientists found the first insights into what stars are composed of. Continuing this research lead to unidentifiable lines in the spectra. Conditions in the interstellar medium(ISM) are responsible for the presence of unstable molecules that do not have the ability to form on earth and studying these molecules experimentally in a lab is very difficult. Alternatively, quantum mechanical and computer models are utilized. As molecules with an increasing number of atoms are studied, these calculations are too computationally expensive to run. To combat this issue, semi-empirical methods are used to cut down the time cost by a tremendous amount. The downside to these methods is that they are not nearly as accurate. By optimizing the parameters of these methods for small molecules first, accurate data that matches the time consuming methods can be obtained. Succeeding with smaller molecules will allow us to run calculations for much larger polycyclic aromatic hydrocarbons(PAHs).

C₃H₂ is small enough to study and also similar to large PAHs so it works as a transition period for us. In the ISM, large PAHs can fraction off into smaller molecules like C₃H₂ which has a larger dipole moment and can be used to detect that larger PAHs are present in a certain region.

Molecules have what are called vibrational modes that are specific to the types and masses of the atoms present. When a molecule’s vibrational modes change the dipole moment, the molecule absorbs a specific wavelength of light that corresponds to the frequency of the vibrational mode. Infrared light corresponds to the transitions of these vibrational modes just like visible light corresponds to electron transitions. Predicting the frequencies allows species to be identified in the ISM.

RMSD (pre-opt) 0.4192 kcal/mol
RMSD (post-opt) 0.0064 kcal/mol

These graphs depict potential energy surfaces for C₃H₂. These are generated by making small displacements in the geometry and calculating the energy associated with that structure. Semi-empirical methods(red curve) use a series of parameters to approximate the electron-electron repulsions within the system which make them less accurate than CCSD(T)/aug-ccpV5Z calculations(black curve) conducted by our collaborators. However, we systematically vary these parameters to allow our data to converge with the data from our collaborators. These surfaces need to be as close as possible before finding the frequencies. Small differences in these surfaces have translated to a large error in the frequencies.

Applications:

Orion Nebula
The Orion Nebula, 1,500 ly away, is the brightest spot in the Orion constellation. Stellar winds from young but massive star clusters create ridges and cavities within the nebula. Astronomers believe it to be the birthplace of more than 1,000 young stars. This region is also believed to contain PAHs.

Vibrant images from the illustrious Hubble Space Telescope present astounding phenomena out in the ISM. However, these images are actually false color. Each color seen in these images is assigned to a detected wavelength in the infrared.

The James Webb Telescope is to be launched and placed above the atmospheric water layer in 2019. This area has been decreasing the accuracy of experimental data.

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Our methods also use these approximations to calculate aspects of the molecule’s geometry. The calculated bond distances and angles using our methods(RM1 shown above) are matched against the ab initio values and the level of error is shown above.

PAHs: polycyclic aromatic hydrocarbons
ISM: interstellar medium