Identifying hexamer structures in alcohol:water mixes

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Caltech CONNECTION

Background

I am working with Sadie Dutton in the Blake group to assist in the analysis of rotational spectra of small-molecule clusters, namely methanol hexamers.

- The goal of this research in the Blake group is to better understand the nature of hydrogen bonding in mixed alcohol:water bulk states. Sadie utilizes chirped pulse Fourier-transform microwave spectroscopy to collect spectra of rotationally cooled alcohol:water clusters. Predictions for rotational constants, and therefore peaks in the spectra, are created by optimizing hypothesized molecular geometries using DFT methods with Gaussian. Then, predictions are matched to experimental data.
- I am utilizing this opportunity to expand my knowledge of areas of research within chemistry and remote sensing, as well as to gain new research skills, including an understanding of remote sensing techniques and computational chemistry programs such as Avogadro and Gaussian.

Approach

1. To assist in building hexamer structures, I utilized the visualization software Avogadro.
2. I began each molecule visualization with a hypothesis of a potential hexamer structure, first creating a sketch, and then building within Avogadro.
3. I delivered molecule files to be run through Gaussian optimization to find the lowest potential energy conformers of the methanol hexamer.
4. Gaussian provided either a final optimized structure, or a failed result, which informed subsequent structure hypotheses.

Figure 1: Sketch of hypothesized prism. Figure 2: Avogadro visualization of prism structure

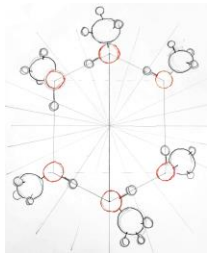

Figure 1

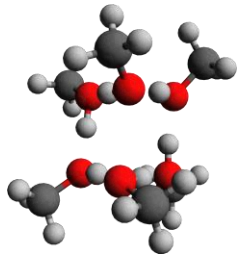

Figure 2

Initial Results

I. Asymmetrical Ring Structure

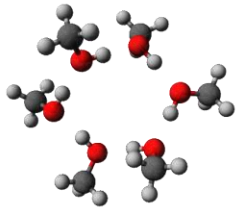

Figure 3
Avogadro visualization of hypothesized hexamer ring.

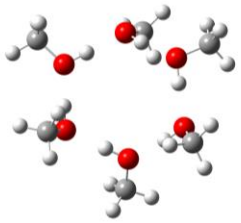

Figure 4
Optimized ring structure; output from Gaussian.

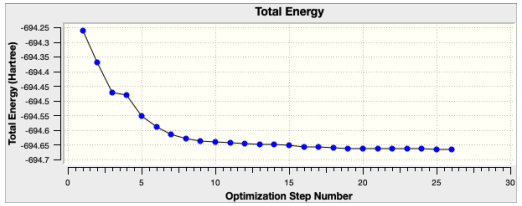

Figure 5
Potential energy plot from initial ring structure to optimized output

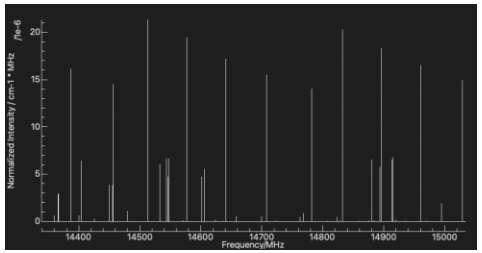

Figure 6
Predictions of peaks in the spectra from calculated rotational constants of optimized structure.

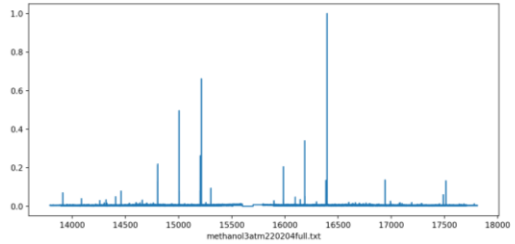

Figure 7
Experimental data showing rotational modes in the spectra.

Conclusions

1. From the computations conducted herein, an asymmetrical ring structure was identified in the experimental data, allowing us to assign and fit observed modes, and thus accurately determine conformer geometry from experimental spectra.
2. Further calculations show that a prism structure is unlikely to exist as a hexamer but may be possible with larger molecules. Future work will aim to identify these higher order prism conformers.

Initial Results

II. Prism Structure

- Initial prism structure hypothesis failed when no potential energy minimum could be found.
- A second prism structure (see Figure 2) optimized to a ring structure which had been previously identified.
- These negative results led us to conclude that a hexamer prism structure is unlikely

III. Educational Outcomes

This work allowed me to develop a deeper understanding about spectroscopy, the scientific process, modeling, and lab work, as well as gain exposure to computational chemistry. Spectroscopy is a key piece of remote detection, an important tool of space science; I learned about the array of types of spectroscopy and how and when they can be applied. Additionally, I gained hands-on experience in research from hypothesis, to modeling, and how these fit into experimental data.

Acknowledgements

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Background image credit: Sadie Dutton