The long term goal of this project is to use absorption measurements of asphaltene-like molecules during their aggregation to determine the evolution of the size and structure of the aggregates during their formation. To do this, we aim to develop a model that uses structural inputs (e.g. relative separation distances, relative molecular orientation, and aggregate size) to simulate the absorption spectra of asphaltene-like molecules. We then aim to incorporate an algorithm that can vary these structural parameters to best fit spectra that have been experimentally measured in situ during aggregation. The last step will be to develop a coarse grained Monte Carlo simulation of asphaltene aggregation to model the structural evolution we extract from the absorption spectra. This year we have made significant progress on the first two aims, and have started preliminary work on the final aim.

Simulating the absorption spectra of asphaltene-like molecules
The structure of pseudoisocyanine (PIC), the asphaltene-like molecule we chose to investigate, is shown in the inset of Figure 1b. The molecule is known to undergo a significant change in its absorption spectrum upon aggregation. We built an instrument that can measure the absorption of these films in situ during aggregation, shown in Figure 1a. The spectra in Figure 1b show the absorption spectra before, during and after molecular aggregation. We observed that there are two stages to molecular aggregation.

We developed code to simulate the absorption spectrum of a molecular aggregate using a Holstein-like Hamiltonian with inputs of electronic and vibrational energy, electronic coupling, aggregate size, and the Huang-Rhys factor. The sign and magnitude of the electronic coupling can be related to the structure of the molecules within the aggregate. We found that the spectra during the aggregation stages could not be simulated by using just one type of aggregate, but instead required both aggregates with positive and negative electronic coupling values, called H and J aggregates, respectively. In response to this finding, we modified our program to simulate the spectrum of a mixture of H and J aggregates. Examples of such simulations are shown in Figure 1b.

Fitting simulated spectra to measured spectra
We wrote an algorithm to vary the simulation parameters to fit experimental spectra. We found that a simple fit of each data point (i.e. optical density as a function of wavelength) did not produce optimal fits. The details of the structure are contained in the energies and relative intensities of the peaks, but the data points conveying this information account for a small fraction of the total number of data points. We devised metrics that contain the information in the experimental spectra which are the most relevant for structure, and determine these metrics for both experimental and simulated spectra. We then vary parameters to fit the metrics of the simulated spectrum to those of the experimental spectrum. This is found to yield simulated spectra that show better agreement with experimental spectra. We found that it is possible to simulate our measured absorption spectra with different combinations of the input parameters. In other words, in the error in the fit is quite flat across a significant region of the parameter space. This means that it is inaccurate to trust any one particular fit of the experimental spectrum. We have devised a method to perform a series of fits with initial guesses for those fits that accurately sample this parameter space. Parameters for simulated spectra that well-fit the experimental spectra are collected in histograms that show the range and likelihood of possible parameter combinations. Figure 2 shows histograms for the number of
molecules in each H- and J-aggregate (n_H and n_J), and the electronic coupling values for each type of aggregate that result in well-fit spectra during molecular aggregation and after aggregation has completed. The apparent change in the electronic coupling values that can possibly result in a good fit indicate that the relative orientation of the molecules within the aggregate and aggregate size change during aggregation.

We have optimized the fit function to create the type of histogram shown in Figure 2 for all of the fit parameters in ~3 hours per absorption spectrum. This will enable fits to many absorption spectra measured in situ, providing insight into the changing structure of the aggregates during aggregation. A preliminary form of this work was published in a conference proceeding, presented at four conferences by the PI, and one conference by a student. A manuscript detailing this work is currently being written up for publication in a peer-reviewed journal.

Coarse-grained Monte Carlo simulations of molecular aggregation

We have also started the next step of this project, simulating the evolving aggregate size distributions using a coarse-grained Monte Carlo simulation. The simulation assumes each molecule in the aggregate is similar to a cube with three types of sides. The three types of cube sides can interact with other cubes, with cubes of solvent, or with a substrate. During each time step in the simulation each individual cube can rotate or move, and aggregates of cubes can move. In this lattice-based model, rotations must occur in 90° steps, and the rotation of a large aggregate is unlikely. Previously, small aggregates of cubes were not allowed to rotate, even though this type of movement is potentially common during aggregation. This year a new student was trained to understand the existing Monte Carlo code and had the chance to exhibit their mastery of the code by implementing a new set of functions and modifying some existing functions to enable small aggregates to rotate during each time step.

Impact of research on personnel

The students funded by this grant have learned how to use a Hamiltonian and dipole operators to compute an absorption spectrum, how to use Monte Carlo code, and how to perform scientific programming. They have learned some of the nuances of programmatically fitting data and how to make code run more efficiently. Both of the students funded by this grant have interest in teaching chemistry as a career path, and this type of research could translate well to a primarily undergraduate institution. We intend to submit an NSF grant on this topic next year, after our peer-reviewed publication is completed, to enable sustained effort on these problems.