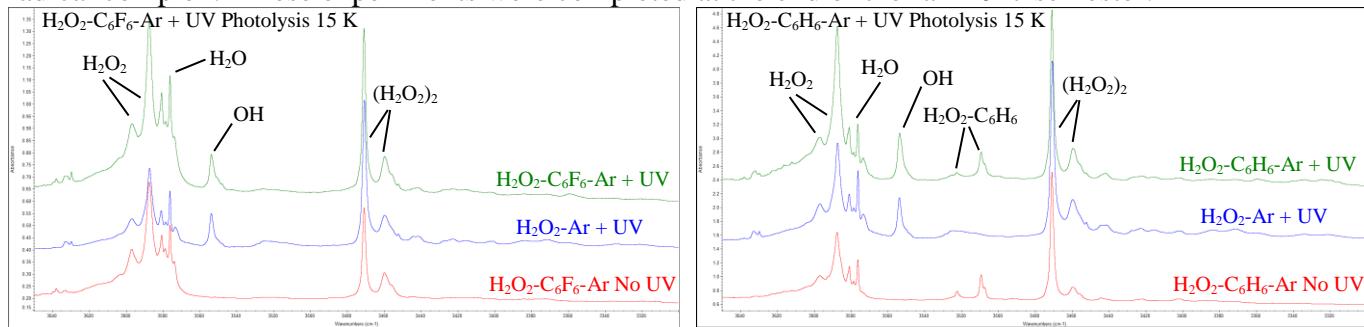


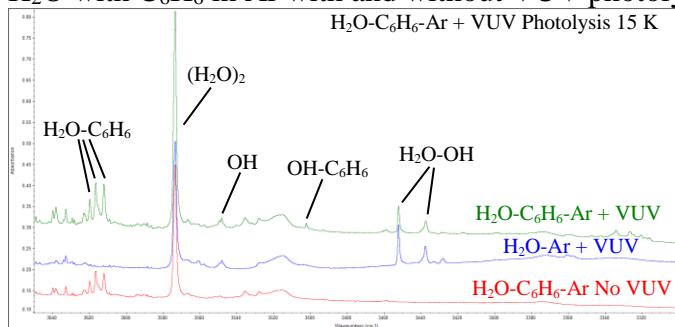
At the time of the last report period (October 1, 2017), I had one undergraduate chemistry major working in my research lab and we were performing experiments to obtain low temperature (15 – 20 K) argon matrices containing hydrogen peroxide (H_2O_2) and then using ultraviolet radiation (200 – 300 nm) to produce the hydroxyl (OH) radical in the argon matrices. The method we were using to obtain the $\text{H}_2\text{O}_2/\text{Ar}$ matrices was by flowing the gaseous Ar over a glass finger containing a solid hydrogen peroxide-urea adduct (H_2O_2 -urea). The urea portion of the adduct is non-volatile at temperatures below 90 °C and therefore the Ar gas only carries the H_2O_2 onto the cold matrix deposition window. The concentration of the H_2O_2 in the argon matrix could be varied by changing the temperature of the solid H_2O_2 -urea adduct from between 20 °C (low concentration) to 40 °C (high concentration). To produce the OH radical, we would simultaneously photolyze the $\text{H}_2\text{O}_2/\text{Ar}$ mixture while depositing on the cold matrix window using the unfiltered light from a 200 W Hg-Xe lamp. Once we had a handle on producing good quality Ar matrices with H_2O_2 and producing the OH radical from the H_2O_2 , we then began working on experiments to produce the OH- C_6F_6 radical complex, which was one of the radical lone pair-pi complexes I had proposed studying for the grant project. This involved performing co-depositions of H_2O_2 with C_6F_6 while simultaneously photolyzing with the Hg-Xe lamp. A series of experiments were performed in which the concentration of both the H_2O_2 and C_6F_6 were varied from high concentration to low concentration. Co-depositions of H_2O_2 with C_6F_6 in Ar were performed both with the Hg-Xe lamp photolysis and without the photolysis in order to identify any peaks in the spectra that might be due to the OH- C_6F_6 radical complex. An example of the spectra for a co-deposition of H_2O_2 with C_6F_6 in Ar with and without Hg-Xe lamp photolysis is shown below. We had performed theoretical calculations at the MP2/aug-cc-pVDZ level for the OH- C_6F_6 radical complex and these predicted that the O-H stretching frequency should be shifted down approximately 12 cm^{-1} from the free OH radical stretch, which occurs at 3554 cm^{-1} . We examined the co-deposition spectra we obtained for the O-H stretching peak of the OH- C_6F_6 radical complex, but unfortunately we were not able to observe any peaks that we could unambiguously assign to the OH- C_6F_6 radical complex. These experiments were completed at the end of the fall 2017 semester.



Given that the OH- C_6F_6 radical complex was an unknown system, I decided that we should try some experiments with a known radical system, namely the OH- C_6H_6 radical complex, which has been produced by Sander and co-workers (*Ang. Chem. Int. Ed.* **2009**, *48*, 4804) using flash vacuum pyrolysis of azobenzene at 500 °C (which produces the phenyl radical) followed by trapping with H_2O in an Ar matrix and then irradiation at 350 nm. In the spring 2018 semester, we began performing co-depositions of H_2O_2 with C_6H_6 in Ar both with the Hg-Xe lamp photolysis and without the photolysis in order to attempt to observe peaks in the IR spectra due to the OH- C_6H_6 radical complex. I had two additional undergraduate students join my research group during the spring 2018 semester for a total of three undergraduate students working with me in my research lab. For these co-depositions, we also performed a series of experiments in which the concentrations of H_2O_2 and C_6H_6 were varied from high concentration to low concentration. An example of the spectra for a co-deposition of H_2O_2 with C_6H_6 in Ar with and without Hg-Xe lamp photolysis is shown above. The most characteristic IR peak of the OH- C_6H_6 radical complex is the O-H stretch, which was reported by Sander and co-workers at 3502.2 cm^{-1} in an Ar matrix. Unfortunately, we were unable to observe the peak 3502.2 cm^{-1} in our experiments, indicating we were not forming the OH- C_6H_6 radical complex in our matrices.

Even though we did not observe the peak at 3502.2 cm^{-1} due to the OH-C₆H₆ radical complex, we did observe a peak at 3509.5 cm^{-1} that was present in the co-deposition spectra without the Hg-Xe lamp photolysis and was not present when either of the monomers was deposited alone. Based on theoretical calculations, we assigned this peak to the H₂O₂-C₆H₆ complex and we were able to observe two other IR peaks for the complex at 1285.8 and 680.5 cm^{-1} . I performed a literature search and discovered that the Ar matrix IR peaks for this complex had not been reported in the literature and so I decided that we should pursue the characterization of this complex further. After the series of H₂O₂ + C₆H₆ co-depositions in Ar had been completed, we synthesized an isotopic hydrogen peroxide-urea sample, which ended up being a mixture of H₂O₂-urea, HDO₂-urea, and D₂O₂-urea, with HDO₂-urea being the deuterium isotope produced in the largest amount. Using this isotopic sample, we were able to characterize the IR peaks of the HDO₂-C₆H₆ complex in an Ar matrix. In addition to the H₂O₂ + C₆H₆ co-depositions in Ar matrices, we also performed H₂O₂ + C₆H₆ co-depositions in nitrogen (N₂) matrices and were able to observe the analogous IR H₂O₂-C₆H₆ complex peaks in N₂ matrices. I presented the work on the H₂O₂-C₆H₆ complex at the 2018 International Symposium on Molecular Spectroscopy conference in June 2018 and one of my undergraduate students presented a poster on the H₂O₂-C₆H₆ complex work in Ar matrices at the Central Regional ACS meeting that was held in Toledo, OH in June 2018.

While we were performing the experiments for the H₂O₂-C₆H₆ complex, we were able to diagnose the problems with our 2450 MHz microwave power supply with the help of our Chemistry Department instrument technician and it was restored back to operational status. All of the original methods I had envisioned to produce the OH radical, which were vacuum-ultraviolet (VUV) photolysis of H₂O, microwave plasma discharge of H₂O, and microwave plasma discharge of H₂ and O₂ mixtures, required the use of the microwave power supply. With it being operational again, near the end of the summer of 2018 we began performing experiments using the vacuum-ultraviolet photolysis source with H₂O to produce the OH radical in Ar matrices and we were able to successfully produce and observe the IR peaks due to the OH radical and the H₂O-OH radical complex in Ar matrices. I decided that we should still focus on the OH-C₆H₆ radical complex, since it has a known O-H stretching peak in Ar, however, before we performed the H₂O + C₆H₆ co-deposition experiments with the VUV photolysis source, we also needed to perform a series of C₆H₆/Ar VUV deposition experiments primarily as control experiments, in which incidentally we were able to observe the production of fulvene, benzvalene, and Dewar benzene based on literature spectra. We completed these experiments at the end of August and over the last few weeks we have been performing the H₂O + C₆H₆ co-deposition experiments with the VUV photolysis source and I am pleased to report that we have been able to observe the 3502.2 cm^{-1} peak due to the OH-C₆H₆ radical complex in our Ar matrices. An example of the spectra for a co-deposition of H₂O with C₆H₆ in Ar with and without VUV photolysis is shown below.



This indicates to me that we can produce a hydroxyl radical-aromatic complex with our matrix isolation system and we should be able to get back to working on our original target radical lone pair-pi systems. However, before we embark on the radical lone pair-pi systems, we will continue to perform the VUV photolysis experiments for the H₂O + C₆H₆ system over the fall 2018 semester to optimize the parameters to produce the highest yield of the OH-C₆H₆ radical complex with this source. In addition, we will also perform other experiments on the H₂O + C₆H₆ system using microwave plasma discharge of H₂O and microwave plasma discharge of H₂ and O₂ mixtures. After this, we will then begin working on VUV photolysis and microwave plasma discharge co-deposition experiments with H₂O and C₆F₆ in Ar in order to attempt to produce and observe the O-H stretching peak for the OH-C₆F₆ radical complex, which was one of the radical lone pair-pi complexes I had proposed studying for the grant project.