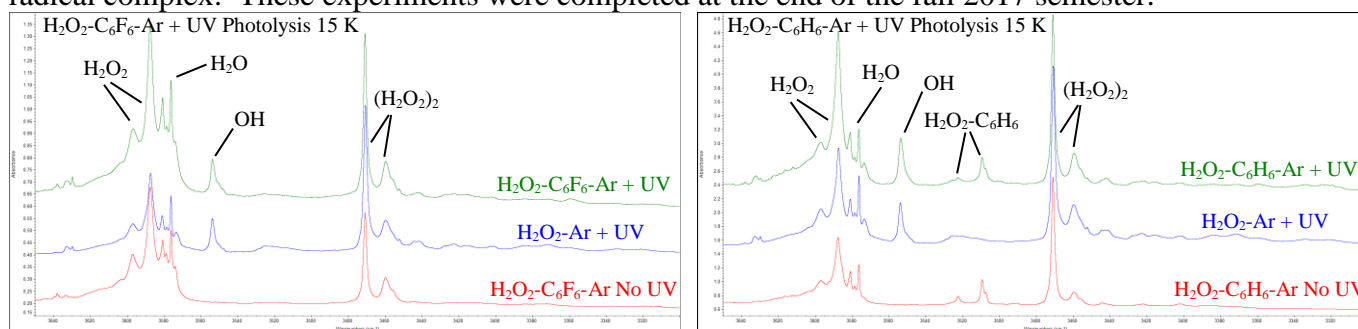


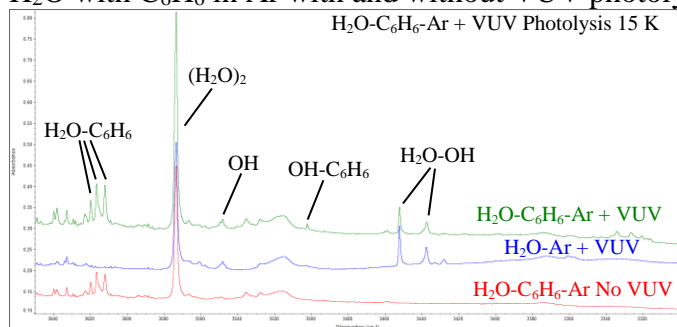
At the time of the last report period (October 1, 2017), I had one undergraduate chemistry major working in my research lab and we were performing experiments to obtain low temperature (15 – 20 K) argon matrices containing hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and then using ultraviolet radiation (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 ( $\text{H}_2\text{O}_2$ -urea). The urea portion of the adduct is non-volatile at temperatures below 90 °C and therefore the Ar gas only carries the  $\text{H}_2\text{O}_2$  onto the cold matrix deposition window. The concentration of the  $\text{H}_2\text{O}_2$  in the argon matrix could be varied by changing the temperature of the solid  $\text{H}_2\text{O}_2$ -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  $\text{H}_2\text{O}_2$  and producing the OH radical from the  $\text{H}_2\text{O}_2$ , we then began working on experiments to produce the OH- $\text{C}_6\text{F}_6$  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  $\text{H}_2\text{O}_2$  with  $\text{C}_6\text{F}_6$  while simultaneously photolyzing with the Hg-Xe lamp. A series of experiments were performed in which the concentration of both the  $\text{H}_2\text{O}_2$  and  $\text{C}_6\text{F}_6$  were varied from high concentration to low concentration. Co-depositions of  $\text{H}_2\text{O}_2$  with  $\text{C}_6\text{F}_6$  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- $\text{C}_6\text{F}_6$  radical complex. An example of the spectra for a co-deposition of  $\text{H}_2\text{O}_2$  with  $\text{C}_6\text{F}_6$  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- $\text{C}_6\text{F}_6$  radical complex and these predicted that the O-H stretching frequency should be shifted down approximately 12  $\text{cm}^{-1}$  from the free OH radical stretch, which occurs at 3554  $\text{cm}^{-1}$ . We examined the co-deposition spectra we obtained for the O-H stretching peak of the OH- $\text{C}_6\text{F}_6$  radical complex, but unfortunately we were not able to observe any peaks that we could unambiguously assign to the OH- $\text{C}_6\text{F}_6$  radical complex. These experiments were completed at the end of the fall 2017 semester.



Given that the OH- $\text{C}_6\text{F}_6$  radical complex was an unknown system, I decided that we should try some experiments with a known radical system, namely the OH- $\text{C}_6\text{H}_6$  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  $\text{H}_2\text{O}$  in an Ar matrix and then irradiation at 350 nm. In the spring 2018 semester, we began performing co-depositions of  $\text{H}_2\text{O}_2$  with  $\text{C}_6\text{H}_6$  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- $\text{C}_6\text{H}_6$  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  $\text{H}_2\text{O}_2$  and  $\text{C}_6\text{H}_6$  were varied from high concentration to low concentration. An example of the spectra for a co-deposition of  $\text{H}_2\text{O}_2$  with  $\text{C}_6\text{H}_6$  in Ar with and without Hg-Xe lamp photolysis is shown above. The most characteristic IR peak of the OH- $\text{C}_6\text{H}_6$  radical complex is the O-H stretch, which was reported by Sander and co-workers at 3502.2  $\text{cm}^{-1}$  in an Ar matrix. Unfortunately, we were unable to observe the peak 3502.2  $\text{cm}^{-1}$  in our experiments, indicating we were not forming the OH- $\text{C}_6\text{H}_6$  radical complex in our matrices.

Even though we did not observe the peak at  $3502.2\text{ cm}^{-1}$  due to the OH-C<sub>6</sub>H<sub>6</sub> radical complex, we did observe a peak at  $3509.5\text{ cm}^{-1}$  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 H<sub>2</sub>O<sub>2</sub>-C<sub>6</sub>H<sub>6</sub> complex and we were able to observe two other IR peaks for the complex at  $1285.8$  and  $680.5\text{ cm}^{-1}$ . 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 H<sub>2</sub>O<sub>2</sub> + C<sub>6</sub>H<sub>6</sub> co-depositions in Ar had been completed, we synthesized an isotopic hydrogen peroxide-urea sample, which ended up being a mixture of H<sub>2</sub>O<sub>2</sub>-urea, HDO<sub>2</sub>-urea, and D<sub>2</sub>O<sub>2</sub>-urea, with HDO<sub>2</sub>-urea being the deuterium isotope produced in the largest amount. Using this isotopic sample, we were able to characterize the IR peaks of the HDO<sub>2</sub>-C<sub>6</sub>H<sub>6</sub> complex in an Ar matrix. In addition to the H<sub>2</sub>O<sub>2</sub> + C<sub>6</sub>H<sub>6</sub> co-depositions in Ar matrices, we also performed H<sub>2</sub>O<sub>2</sub> + C<sub>6</sub>H<sub>6</sub> co-depositions in nitrogen (N<sub>2</sub>) matrices and were able to observe the analogous IR H<sub>2</sub>O<sub>2</sub>-C<sub>6</sub>H<sub>6</sub> complex peaks in N<sub>2</sub> matrices. I presented the work on the H<sub>2</sub>O<sub>2</sub>-C<sub>6</sub>H<sub>6</sub> complex at the 2018 International Symposium on Molecular Spectroscopy conference in June 2018 and one of my undergraduate students presented a poster on the H<sub>2</sub>O<sub>2</sub>-C<sub>6</sub>H<sub>6</sub> 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 H<sub>2</sub>O<sub>2</sub>-C<sub>6</sub>H<sub>6</sub> 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 H<sub>2</sub>O, microwave plasma discharge of H<sub>2</sub>O, and microwave plasma discharge of H<sub>2</sub> and O<sub>2</sub> 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 H<sub>2</sub>O 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 H<sub>2</sub>O-OH radical complex in Ar matrices. I decided that we should still focus on the OH-C<sub>6</sub>H<sub>6</sub> radical complex, since it has a known O-H stretching peak in Ar, however, before we performed the H<sub>2</sub>O + C<sub>6</sub>H<sub>6</sub> co-deposition experiments with the VUV photolysis source, we also needed to perform a series of C<sub>6</sub>H<sub>6</sub>/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 H<sub>2</sub>O + C<sub>6</sub>H<sub>6</sub> co-deposition experiments with the VUV photolysis source and I am pleased to report that we have been able to observe the  $3502.2\text{ cm}^{-1}$  peak due to the OH-C<sub>6</sub>H<sub>6</sub> radical complex in our Ar matrices. An example of the spectra for a co-deposition of H<sub>2</sub>O with C<sub>6</sub>H<sub>6</sub> 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 H<sub>2</sub>O + C<sub>6</sub>H<sub>6</sub> system over the fall 2018 semester to optimize the parameters to produce the highest yield of the OH-C<sub>6</sub>H<sub>6</sub> radical complex with this source. In addition, we will also perform other experiments on the H<sub>2</sub>O + C<sub>6</sub>H<sub>6</sub> system using microwave plasma discharge of H<sub>2</sub>O and microwave plasma discharge of H<sub>2</sub> and O<sub>2</sub> mixtures. After this, we will then begin working on VUV photolysis and microwave plasma discharge co-deposition experiments with H<sub>2</sub>O and C<sub>6</sub>F<sub>6</sub> in Ar in order to attempt to produce and observe the O-H stretching peak for the OH-C<sub>6</sub>F<sub>6</sub> radical complex, which was one of the radical lone pair-pi complexes I had proposed studying for the grant project.