

Research Program: The Loomis research group is building and developing a research program that aims to characterize halogen-bonding and charge-transfer (CT) systems. Specifically, four different binary complexes, the $\text{Br}_2 \cdots \text{H}_2\text{O}$, $\text{Br}_2 \cdots \text{pyridine}$, $\text{Br}_2 \cdots \text{pentafluoropyridine}$, and $\text{Br}_2 \cdots 3\text{-bromotetra-fluoropyridine}$ complexes, will be stabilized, spectroscopically characterized, and the reaction products formed following photoexcitation will be identified. There are several milestones that must be achieved to complete these goals. 1) The pre-reactive complexes must be stabilized, and their formation must be verified spectroscopically, either with laser-induced fluorescence (LIF) or ion detection. 2) The ion time-of-flight (i-TOF) velocity map imaging (VMI) and ionization schemes must be optimized so that only those products generated from the complex of interest are detected, and not higher-order complexes or those with other moieties bound to the complex. 3) The yields of the different product channels will be mapped as a function of excitation energy, spanning from the region of the low-lying Br_2 B state to the higher-energy CT states that are formed with complexation. 4) The dynamics will be monitored in real time using ultrafast pump-probe schemes with i-TOF and VMI detection. By studying halogen bonding with this bottom-up approach, the group will strive to develop fundamental understandings about this class of chemical interaction that has important roles in an array of syntheses and materials components.

Research Progress: During the first funding period of this ACS PRF ND award, the Loomis group has primarily worked on 1) and 2), described above. The efforts were initially centered on stabilizing and spectroscopically characterizing the $\text{Br}_2 \cdots \text{H}_2\text{O}$ and $\text{Br}_2 \cdots \text{pyridine}$ systems. When utilizing a simple pulsed valve as the expansion source, no signals that could be associated with the complexes could be identified in either LIF spectra or ion spectra. This is despite the fact that the intensity of the Br_2 features would dramatically decrease, suggesting the Br_2 molecules are either stabilized in clusters or undergoing reaction. It quickly became evident that some reaction does occur prior to the expansion, and it would be necessary to incorporate a mixing nozzle, where the two moieties would only be introduced to each other just prior to the expansion in order to minimize reaction. The LIF spectra collected with two different designs of mixing nozzles using Br_2 and pyridine entrained in separate helium carrier gas flows contain large continuum fluorescence signals through the Br_2 B-X spectral region. The relative intensities of this continuum relative to the Br_2 and $\text{He} \cdots \text{Br}_2$ spectral features varied between scans and even during the collection of a single scan. The signal intensities also exhibited a large dependence on the relative pressures of the two sources and on the concentrations of the Br_2 and pyridine.

In order to optimize the operation of the mixing nozzles, and to gain a better handle on the parameters required to stabilize these halogen bonding systems, the efforts were stepped back and experiments on the $\text{I}_2 \cdots \text{pyridine}$ complex were undertaken. This I_2 system is less reactive and should be easier to work with from a practical perspective as iodine is a solid at room temperature, and its vapor pressure can easily be adjusted by varying the temperature of the iodine sample vessel. Spectral data on $\text{I}_2 \cdots \text{pyridine}$ are now being collected. As with the spectra recorded of the $\text{Br}_2 \cdots \text{H}_2\text{O}$ and $\text{Br}_2 \cdots \text{pyridine}$ complexes, the preliminary LIF spectra of $\text{I}_2 \cdots \text{pyridine}$ recorded in the I_2 B-X spectral region contain continuum signals with weak maxima located near each of the I_2 monomer transitions, as shown in **Figure 1**. The features in the LIF spectra are less sensitive to the expansion conditions, but day-to-day reproducibility of the spectra remains a challenge. To better identify the origin of the continuum signals, two-laser experiments will be performed to identify the origin of the fluorescence signals. In addition, complementary i-TOF spectra will be recorded to identify if electronic predissociation or chemical reaction is occurring after excitation of the complexes. Note it is unlikely that the continuum signals could

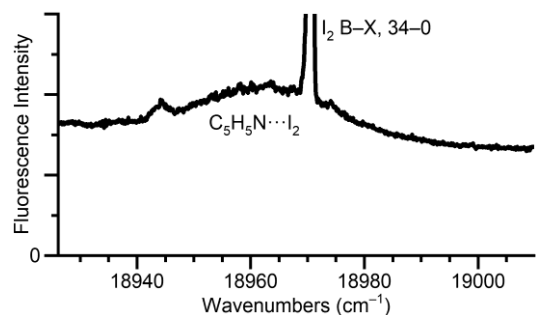


Figure 1. LIF spectrum recorded in the I_2 B-X, 34-0 spectral region and with a co-expansion of pyridine ($\text{C}_5\text{H}_5\text{N}$) and I_2 in a late mixing nozzle. There is a large continuum fluorescence signal throughout the B-X spectral region.

be attributed to CT states as these excitation energies are significantly lower than expected.

Tune-up experiments for those that will probe the chemical reaction products of the bromine complexes using i-TOF and VMI are underway. Due in part to the temporary shift towards investigating the $I_2 \cdots$ pyridine system, the apparatus has been optimized for the detection of I atoms. Specifically, experiments are being performed on $Ar \cdots I_2$ complexes. Here, different intermolecular vibrational levels are prepared within the $Ar + I_2(B, v')$ potential energy surfaces, and the formation of I atoms are monitored with VMI. The I atoms can only be formed via electronic predissociation (EP). Numerous research groups investigating rare gas atom \cdots dihalogen complexes have deduced that EP can effectively compete with fluorescence and vibrational predissociation of the excited-state complexes. The efficiency of EP should be largest for the heavier more polarizable rare gas atoms. Direct detection of the EP products has not been reported, it has only been inferred.

Thus far, the $He \cdots I_2$, $Ne \cdots I_2$, $Ar \cdots I_2$, $He \cdots Br_2$, and $Ar \cdots Br_2$ complexes have been investigated, and the only system for which we have identified the EP mechanism is $Ar \cdots I_2$. The efficiency of EP for $Ar \cdots I_2$ is oscillatory with increasing I_2 vibrational excitation in the B state, v' . The anisotropy of the I^+ images, with anisotropy parameters of $\beta = 0.2$ to 0.5 , indicate that the EP is prompt in comparison to the rotational motion of the complexes. By integrating over the angular coordinate of the I^+ images, the kinetic energy distributions of the I-atom products, $KE(I)$, can be obtained. As shown in **Figure 2**, the shapes of the $KE(I)$ depend on v' . Most of the distributions appear Lorentzian with a single maximum, as shown at the top for $v'=12$. This is what one would expect for prompt three-body dissociation of a rigid T-shaped $Ar \cdots I_2$ complex into separate $Ar + I + I$ atomic fragments. The $KE(I)$ for some of the levels, such as the $v'=14$ and 20 levels, exhibit multiple local maxima, which represents the two dissociating I atoms are experiencing dissimilar forces and environments. (Some of the I atoms are formed with higher and some with lower kinetic energies.) These $KE(I)$ provide evidence that some of the initially prepared $Ar \cdots I_2$ complexes, which have rigid a C_{2v} symmetry may be coupled to other intermolecular vibrational levels that deviate away from the T-shaped geometry, likely through intramolecular vibrational energy redistribution. This manuscript is currently in preparation.

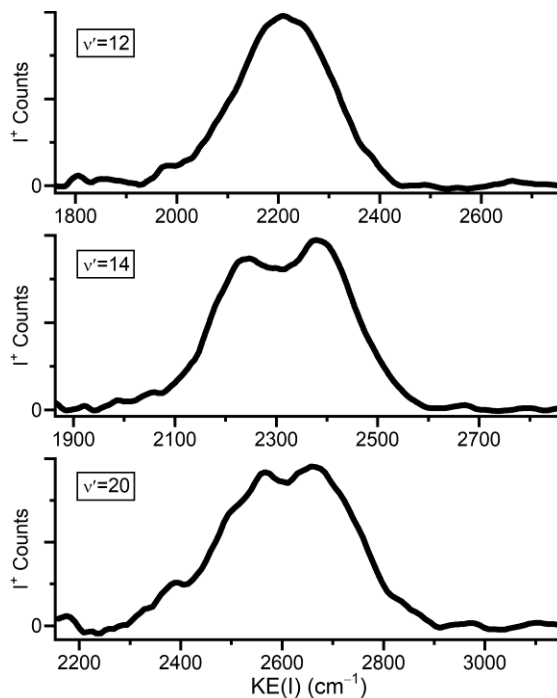


Figure 2. Kinetic energy distributions, $KE(I)$, obtained from the I^+ cation images generated by ionizing the I-atom fragments formed via electronic predissociation of the $Ar \cdots I_2$ complexes prepared in the T-shaped levels bound within the $Ar + I_2(B, v')$ potential energy surfaces.

Impact of the Research: This ACS PRF ND award has proven to be a lifeline for the gas-phase dynamics efforts in the Loomis laboratory. There is a concerted and calculated effort to transform the research program from one focused on characterizing intermolecular interactions within rare gas \cdots dihalogen complexes to the investigation of chemical reactions and halogen bonding. To do this, numerous modifications to the apparatus have been made, including the incorporation of mixing nozzles to stabilize the complexes and the modification of the i-TOF apparatus to handle higher gas throughputs. Although, funding through several other sources have been sought, there is a need to obtain preliminary results to provide proof-of-principle results and to better convey the dynamics that can be learned.

Although the investigations into halogen bonding in the Br_2 complexes is just getting going, two graduate students have already benefited from the ACS PRF ND award. This award has given them an opportunity to design, build, and incorporate numerous components on the apparatus. These skills and experiences will help them greatly in their career endeavors. In addition, there is nothing like inconsistent results to help tune one's scientific method by trouble shooting chemical systems. At the same time, the successes achieved on the EP of T-shaped $Ar \cdots I_2$ complexes have not only given the students senses of accomplishment, the results will address a hole in the cluster community, the lack of direct evidence for EP in the rare gas \cdots dihalogen complexes, that has existed for nearly fifty years. The skills developed in these studies will be directly utilized when investigating halogen bonding in the Br_2 clusters.