"Characterization of Reaction Dynamics and Interactions Using a Bottom-up Approach"

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Overview of Research Program: The Loomis research group is developing a research program focused on characterizing halogen-bonding and charge-transfer (CT) systems. During the first year, we focused on stabilizing, spectroscopically characterizing, and probing the reaction products formed following photoexcitation of four different binary complexes, the $Br_2 \cdots H_2O$, $Br_2 \cdots$ pyridine, $Br_2 \cdots$ pentafluoropyridine, and $Br_2 \cdots$ 3-bromotetra-fluoropyridine complexes. These experiments ended up being difficult to perform and the data were difficult to analyze as two generalizations were observed. 1) It appeared as though a significant amount of reaction proceeded prior to the supersonic expansion, and numerous products were detected, even without photoexcitation to the CT band. 2) When the detection of the products was minimized, the prominent product detected following photoexcitation was ground-state $Br_2(X,v'')$ molecules with vibrational excitation, $v''>0$. We spent a significant amount of time into the second year of funding trying to optimize the parameters of a mixing nozzle to introduce the reactants during the expansion used to stabilize them in order to minimize undesired reactions. It was difficult to obtain consistent and reproducible results. For these reasons, we have taken a step back during this second year to look at less reactive halogen-bonded systems, reaction pairs including the electron acceptor I_2 instead of Br_2, and those that have been studied previously. Specifically, we began investigating the $I_2 \cdots$ ethylene, $I_2 \cdots$ benzene, and $I_2 \cdots$ pyridine pre-reactive complexes. The naïve goal was to optimize the conditions for stabilizing halogen-bonded complexes, to develop strategies for identifying and characterizing the CT products, and to build upon and expand the understanding of these halogen-bonded systems before returning to the more reactive systems. These investigations are yielding unexpected and interesting results.

Research Progress: Most of the efforts have involved stabilizing and spectroscopically characterizing the $I_2 \cdots$ ethylene ($I_2 \cdots C_2H_4$) CT system due to the simplicity of the system, our successes in identifying product channels, and the ability to compare our results with those recently published.[Bogomolov, et al. *J. Chem. Phys.* **2017**, *147*, 234304] We used an apparatus designed that enabled both laser-induced fluorescence (LIF) spectroscopy and ion time-of-flight velocity-map imaging (VMI) to be performed. LIF spectra were recorded downstream (~2 cm) from the pulsed supersonic expansion used to stabilize the clusters in order to characterize and optimize the expansion conditions. The CT reactions were photoinduced and the fragments were probed further downstream after the expansions entered the VMI region of the apparatus and a molecular beam was formed.

Following the experiments and methodology of Bogomolov, et al, we initially used resonance-enhanced multi-photon ionization (REMPI) and VMI to probe the products formed after photoexcitation in the wavelength region expected for the CT band using a single nanosecond laser and color (~277 nm or ~36,000 cm^{-1}). Surprisingly, we obtained very different results than they reported. They found the major product to be translationally hot, ground-state I_2 molecules with significant vibrational excitation. Under no conditions did we detect any I_2 fragments that could be attributed to photoexcitation of $I_2 \cdots C_2H_4$ complexes. Instead, we detected both $I(^2P_{3/2})$ and $I(^2P_{1/2})$ atomic fragments. The kinetic energies of the $I(^2P_{3/2})$ fragments formed and detected with five different photon energies are plotted in **Figure 1** (top). The distributions are quite broad, and they extend to very high kinetic energies. The total kinetic energy available can
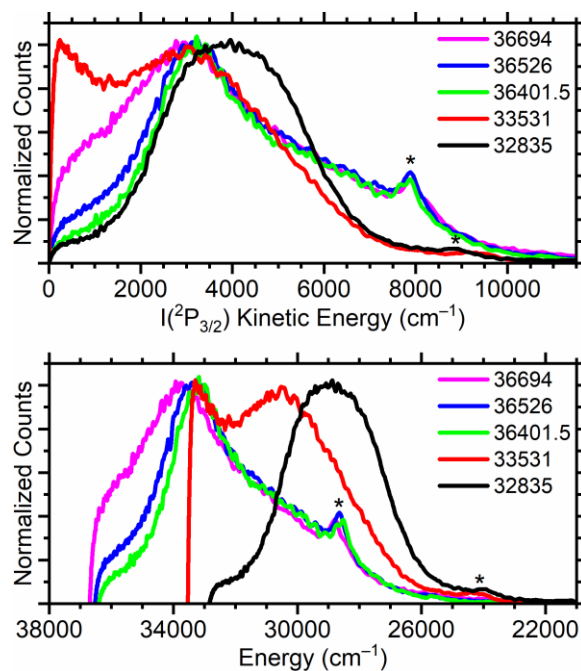

Figure 1. Kinetic energy distributions of $I(^2P_{3/2})$ products formed with the indicated photon energies used to promote $I_2 \cdots C_2H_4$ complexes to the CT region. The same photon energies were used for (2+1) REMPI of the atoms. (Top) The distributions obtained directly from the VMI data. (Bottom) The distributions replotted as a function of photon energy minus the kinetic energy of the $I(^2P_{3/2})$ products. The peaks marked with an * are associated with atoms formed by photodissociation of I_2 molecules.

be estimated by subtracting the calculated binding energy of the ground-state $I_2 \cdots C_2H_4$ complex, 1,460 cm^{-1},[Kalume, et al. *J. Phys. Chem. A* **2014**, *118*, 6838] and the energetic asymptote of the $I(^2P_{3/2}) + I(^2P_{1/2})$ channel, 20,043 cm^{-1}, from the excitation energy. Thus, the total energy available for these data range from 11,332 to 15,191 cm^{-1}. Similar experiments were performed probing the formation of $I(^2P_{1/2})$ products. Negligible signals were detected for photon energies < 33,000 cm^{-1}. In addition, the kinetic energies were much lower in energy, < 4,000 cm^{-1} and much narrower than the $I(^2P_{3/2})$ distributions. There was noticeably no $I(^2P_{1/2})$ products with kinetic energies < 2,000 cm^{-1}.

The interpretation of the measured $I(^2P_{3/2})$ and $I(^2P_{1/2})$ product kinetic energy distributions was not obvious at first. However, by plotting the distributions as a function of energy below the excitation energy, **Figure 1** (bottom), it is noticeable that an additional reaction pathway that produces atoms with lower kinetic energies opens for energies > 33,000 cm^{-1}. These pathways are indicated in **Figure 2**. At lower excitation energies, the initially prepared CT complex couples to a repulsive state, likely the $I_2(^3\Sigma_u^+{}_{(0-)})$ state. One $I(^2P_{3/2})$ atom comes off translationally hot, and the second interacts with the C_2H_4 molecule, forming a metastable radical. The excess energy in the radical results in dissociation and the formation of a second $I(^2P_{3/2})$ atom with less kinetic energy, which results in a very broad distribution. At higher excitation energies, the CT state couples with a different dissociative state, and one $I(^2P_{1/2})$ atom is formed with a narrow kinetic energy distribution. The metastable radical dissociates forming an $I(^2P_{3/2})$ atom with very little kinetic energy.
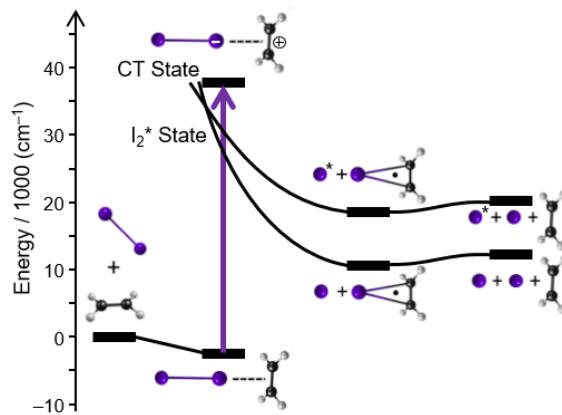

Figure 2. Schematic of the reaction pathways experimentally observed after photoexcitation to the CT state of $I_2 \cdots C_2H_4$. This figure was modified from Kalume, et al. *J. Phys. Chem. A* **2014**, *118*, 6838.

In order to better map out the competing reaction pathways, we have begun experiments using two nanosecond lasers and two colors. The wavelength of the REMPI laser remains fixed on either a $I(^2P_{3/2})$ or a $I(^2P_{1/2})$ 2+1 ionization transition. We are systematically tuning the excitation energy to access and identify the different reaction pathways within the CT band. The first I atoms are formed on very short timescales, and the anisotropy of these signals provides a handle on the symmetry of the state that is accessed with excitation. The anisotropy of the signals associated with the second atoms are approximately zero, which we associate with a much longer timescale for forming these products.

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. This award is enabling our efforts to transform our chemical reaction dynamics 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 were made, including the lengthening of the time-of-flight region to gain momentum resolution, the modification of the apparatus to handle higher gas throughputs, and the incorporation of mixing nozzles to stabilize the complexes. 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.

Thus far, three graduate students and one undergraduate student have 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. Due to our results not resembling those in the literature, we have performed an extensive list of verification experiments, such as recording data with varied molecular concentrations and supersonic expansion conditions, as well as varying excitation and ionization laser energies and fluences. We predict future experiments performed using other electron donor molecules may result in different dynamics as the coupling with the many I_2 repulsive states will depend on the molecule's structure and electronic properties. We do not want to wait too long before returning to more reactive systems, such as those including Br_2. We are also looking forward to performing these experiments with femtosecond lasers, instead of with nanosecond lasers, so that the dynamics can be probed in real time. The ability to map out with both energy and temporal resolution should provide benchmarks for theory and insights for chemical reactions in the condensed phase.