LOW-TEMPERATURE REACTION KINETICS USING CHIRPED PULSE ROTATIONAL SPECTROSCOPY

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In the past few years, the Suits group has successfully adapted the chirped-pulsed rotational spectroscopy technique to study reaction dynamics. A clear advantage of this method is its ability to simultaneously detect the appearance/disappearance of products/reactants of reactions within the frequency range of a single chirp. However, kinetic studies require a well-known, uniform density and temperature environment throughout the course of the reaction. Our Chirped Pulse Uniform Flow (CPUF) spectrometer achieves these conditions by the uniform supersonic flow produced from a Laval nozzle expansion following the pioneering CRESU technique developed in France. However, high densities in the uniform flow (10^{14} – 10^{17} molecules/cm^3) can attenuate the molecular coherence through collisions and therefore limit the MW/mmW spectroscopic detection.

To overcome this, we adapted an airfoil sampling technique in which the reaction takes place in the uniform supersonic flow and then expands into a cold, low-density sampling region that is optimal for MW/mmW spectroscopic detection. This airfoil sampling CPUF spectrometer, in the 70 – 90 GHz range, has been used to study the low-temperature kinetics of bimolecular reactions and preliminary results will be presented. Initiated by a pulsed photolysis laser at 193 nm, appearance of products/disappearance of reactants have been probed as a function of time with a 5 μs resolution. The data were fitted to pseudo first-order or second-order rate equations to determine the rate constants for chemical reactions.