DYNAMIC TIME-RESOLVED CHIRPED-PULSE ROTATIONAL SPECTROSCOPY OF VINYL CYANIDE PHOTO-PRODUCTS IN A ROOM TEMPERATURE FLOW REACTOR

DANIEL P. ZALESKI, <u>KIRILL PROZUMENT</u>, Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL, USA.

Chirped-pulsed (CP) Fourier transform rotational spectroscopy invented by Brooks Pate and coworkers a decade ago is an attractive tool for gas phase chemical dynamics and kinetics studies. A good reactor for such a purpose would have well-defined (and variable) temperature and pressure conditions to be amenable to accurate kinetic modeling. Furthermore, in low pressure samples with large enough number of molecular emitters, reaction dynamics can be observable directly, rather than mediated by supersonic expansion. In the present work, we are evaluating feasibility of *in situ* time-resolved CP spectroscopy in a room temperature flow tube reactor. Vinyl cyanide (CH₂CHCN), neat or mixed with inert gasses, flows through the reactor at pressures $1 - 50 \ \mu$ bar ($0.76 - 38 \ m$ Torr) where it is photodissociated by a 193 nm laser. Millimeter-wave beam of the CP spectrometer co-propagates with the laser beam along the reactor tube and interacts with nascent photoproducts. Rotational transitions of HCN, HNC, and HCCCN are detected, with $\geq 10 \ \mu$ s time-steps for 500 ms following photolysis of CH₂CHCN. The post-photolysis evolution of the photoproducts' rotational line intensities is investigated for the effects of rotational and vibrational thermalization of energized photoproducts. Possible contributions from bimolecular and wall-mediated chemistry are evaluated as well.