

DETECTION OF NASCENT PRODUCTS FROM THE PHOTOLYSIS OF ACRYLONITRILE VIA TIME-RESOLVED MILLIMETER WAVE SPECTROSCOPY

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In 2017, we presented at ISMS a new Time-Resolved Kinetic Chirped-Pulse (TReK-CP) spectrometer.^a By coupling a UV photolysis source to a chirped pulse millimeter-wave (mm-wave) spectrometer, we demonstrated the ability to measure kinetic and thermodynamic properties of the photolysis of acrylonitrile (CH₂CHCN), including product branching ratios and rotational and vibrational thermalization rates at reasonable time resolution (ca. 10 μs). However, sensitivity to vibrationally excited states and pre-collisional dynamics was limited, so the observation of truly nascent molecules was still out of reach.

Here, we present improvements to the TReK-CP design that enables detection of nascent product molecules from the photolysis of acrylonitrile, with particular focus on the formation of cyanoacetylene (HC₃N). Moving to the 260-295 GHz mm-wave band significantly improves sensitivity to small polyatomics, enabling detection of HC₃N within 1 μs after photolysis in a variety of vibrational states. We have also devised a new detection scheme that enables a time resolution of 1 μs, amongst other improvements.

Revisiting the photolysis of acrylonitrile with these improvements has led to surprising observations. We will present evidence that HC₃N has different dynamics than the primary photoproduct, HCN, which clearly forms rotationally hot and is undetectable until the first collisional event takes place. Meanwhile, cyanoacetylene forms slower, exhibiting low temperature state distributions, a large kinetic isotopic effect, and strong kinetic dependence on the initial temperature of the precursor. This is consistent with the theoretical prediction that the final step, CH₂CCN → HC₃N + H, occurs with little excess energy.^b We will also show that we are, in fact, detecting truly nascent cyanoacetylene, in that the kinetics show a distinct change from first to second order on the collisional timescale of the reactor.

^aZaleski, D. P.; Prozument, K.; *ISMS 2017, WH02*.

^bZaleski, D. P.; Harding, L. B.; Klippenstein, S. J.; Ruscic, B.; Prozument, K. *J. Phys. Chem. Lett.* **2017**, *8*, 6180.