Detection of astrochemically relevant reaction products in skimmer sampled uniform supersonic flows using chirped pulse Fourier transform mm-wave spectroscopy

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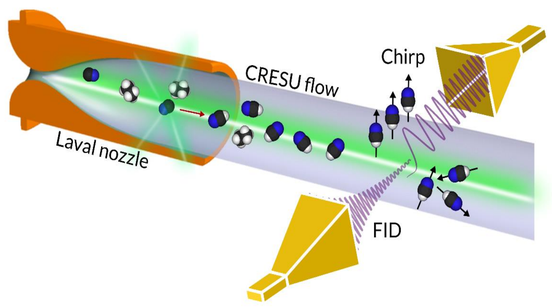
Introduction

- CRESU (Reaction Kinetics in Uniform Supersonic Flow) technique is coupled with the Chirped Pulse Fourier Transform Micro-(mm-)Wave (CPFTMW) spectroscopy technique
- Aim is to study low temperature gas phase collisional processes and determination of branching ratios of multichannel reactions in the interstellar medium

❑ CRESU Technique

Transfer of heat to kinetic energy through an isentropic expansion of a gas via a convergent-divergent Laval nozzle creating a low temperature flow with uniform conditions



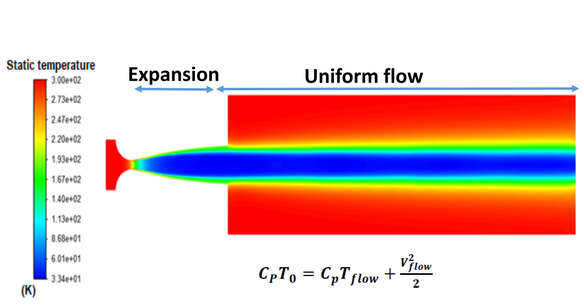


Figure 1. Temperature profile from isentropic expansion

❑ Chirped pulse

- Excitation of dipole molecules within the frequency range of the pulse
- Record the free induction decay (FID)
- Fourier transform of the FID gives the spectrum

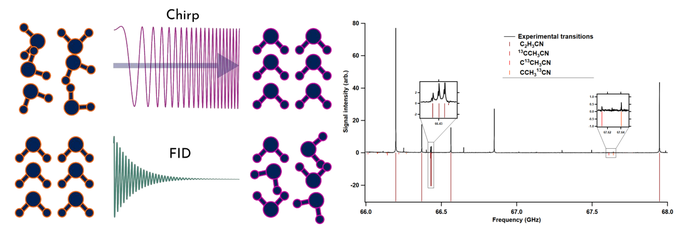


Figure 2. Chirped-pulse technique

❑ Pressure broadening

- Relatively high pressure generated in the CRESU flow
- High collision rate between the radiating molecules and the buffer gas
- Quenched FIDs and weak molecular signal

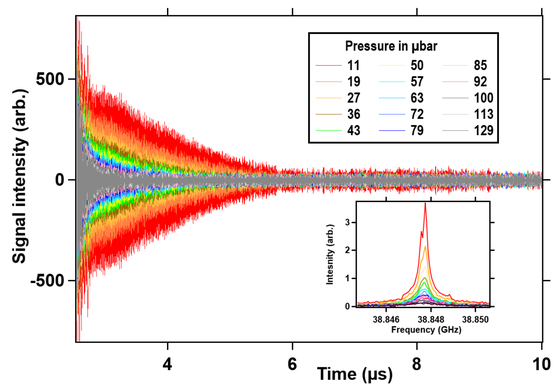
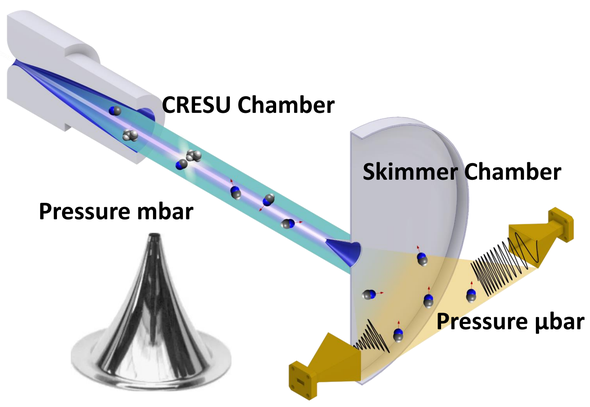


Figure 3. Vinyl cyanide FIDs and associated spectra with increasing pressures in a helium flow at room temperature

Skimmed CRESU setup

- To improve the sensitivity of the technique, the CRESU flow is sampled via a skimmer into a new probing chamber under constant pumping
- The gas re-expands into a nearly collision free environment
- The pressure in the skimmer chamber can be lowered by orders of magnitude depending on the skimmer orifice, the flow conditions and the nature of the buffer



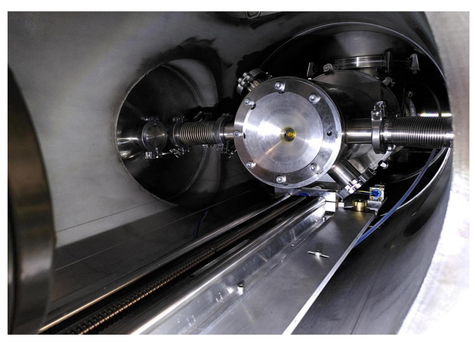


Figure 4. skimmer chamber

- The skimmer geometry and its support are designed to avoid any perturbations of the CRESU flow conditions before reexpanding into the skimmer chamber
- CFD simulations were carried out to optimize the skimmer support profile

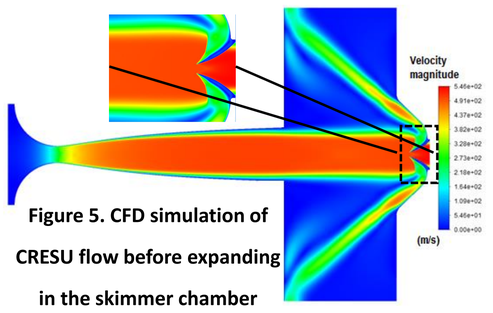


Figure 5. CFD simulation of CRESU flow before expanding in the skimmer chamber

- The characterization of the post-skimmer expansion conditions was conducted via direct simulation Monte-Carlo (DSMC) calculations using DS2V program (Bird 1994)

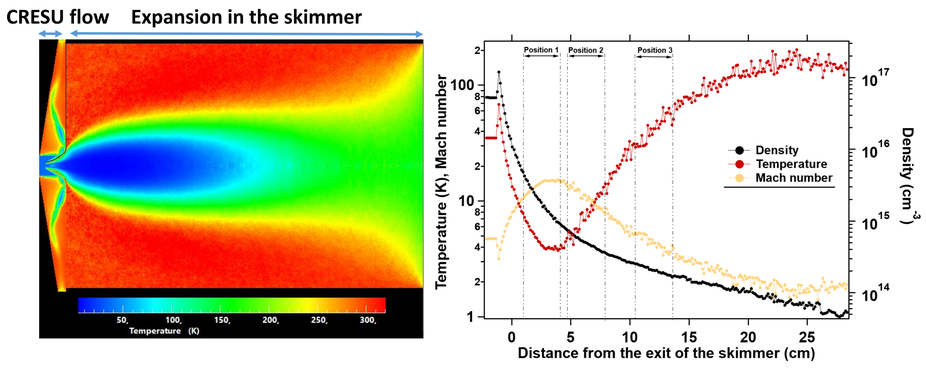


Figure 6. DSMC simulation of the flow conditions in the skimmer chamber

- The rotation diagram was made from a vinyl cyanide spectrum recorded from a chirp in the skimmer chamber to experimentally measure the rotational temperature of the gas expanding from an argon flow at 35 K

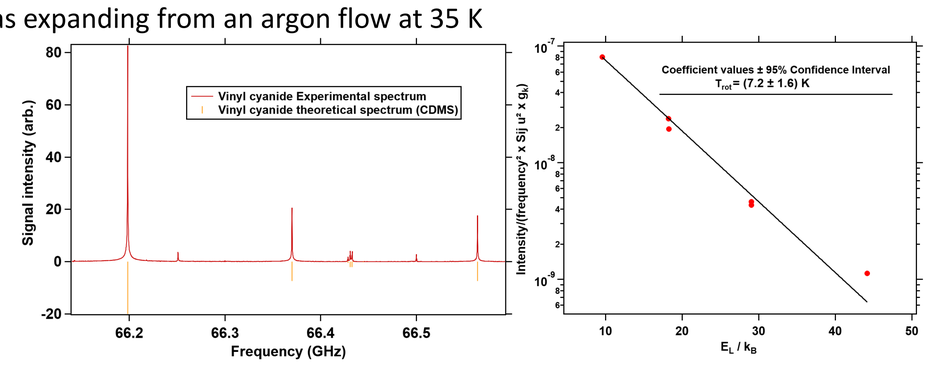


Figure 7. Rotation diagram from vinyl cyanide spectrum under skimmer conditions

Experimental Results

- Comparison of a vinyl cyanide FID and spectrum taken under the skimmer and the CRESU conditions highlights the power of the skimmer. The results from the skimmer chamber give longer FID and show an improvement of the SNR

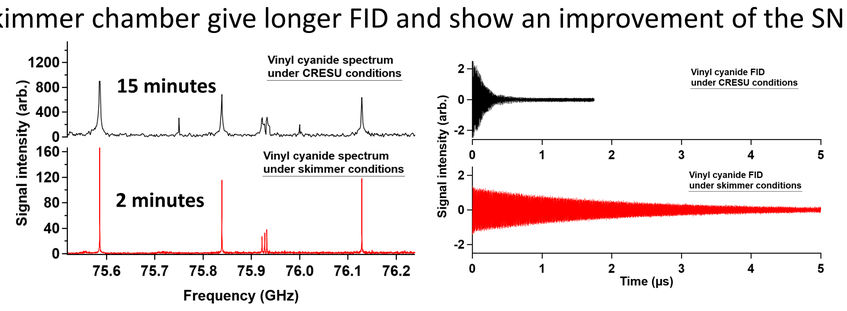


Figure 8. Comparison of vinyl cyanide spectrum and FID under CRESU and skimmer conditions

- Probing of HC_3N as a product from the photolysis of vinyl cyanide at 193 nm in an argon flow at 35 K sampled via a 4 mm skimmer

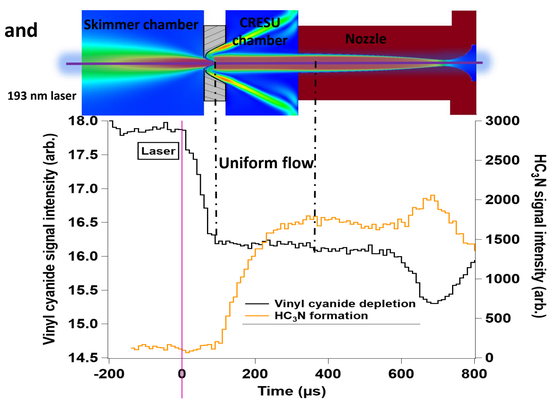


Figure 9. Photolysis of vinyl cyanide

- Two reactions have been studied, CN+C_2H_2 a single channel reaction that yields HC_3N as a product. The second is CN+C_2H_4 which is potentially a dual channel reaction with vinyl cyanide from the first channel and HCN from the second channel used as probing molecules

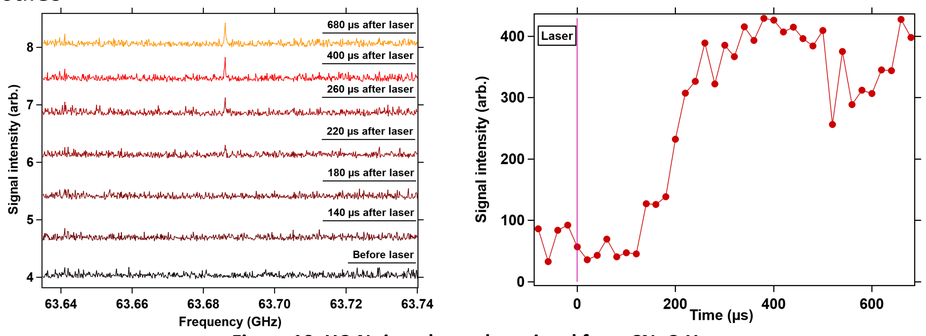


Figure 10. HC_3N time dependent signal from CN+C_2H_2

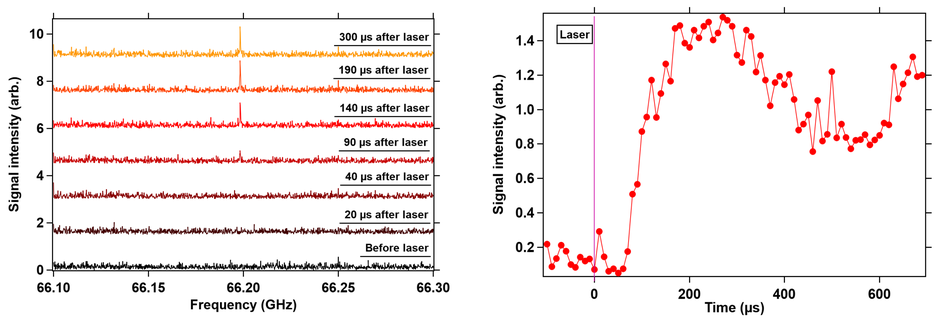
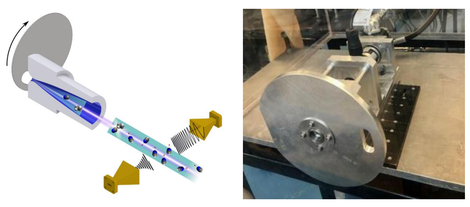


Figure 11. Vinyl cyanide time dependent signal from CN+C_2H_4

Future work

- Increase the pumping efficiency by pulsing the CRESU flow via an aerodynamic chopper
- The gain on pressure is determined by the geometry of the disk
- Spectroscopic probing in the reaction environment



Acknowledgments

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