

Quantitative product branching for multichannel reactions using chirped pulse spectroscopy in pulsed uniform flow



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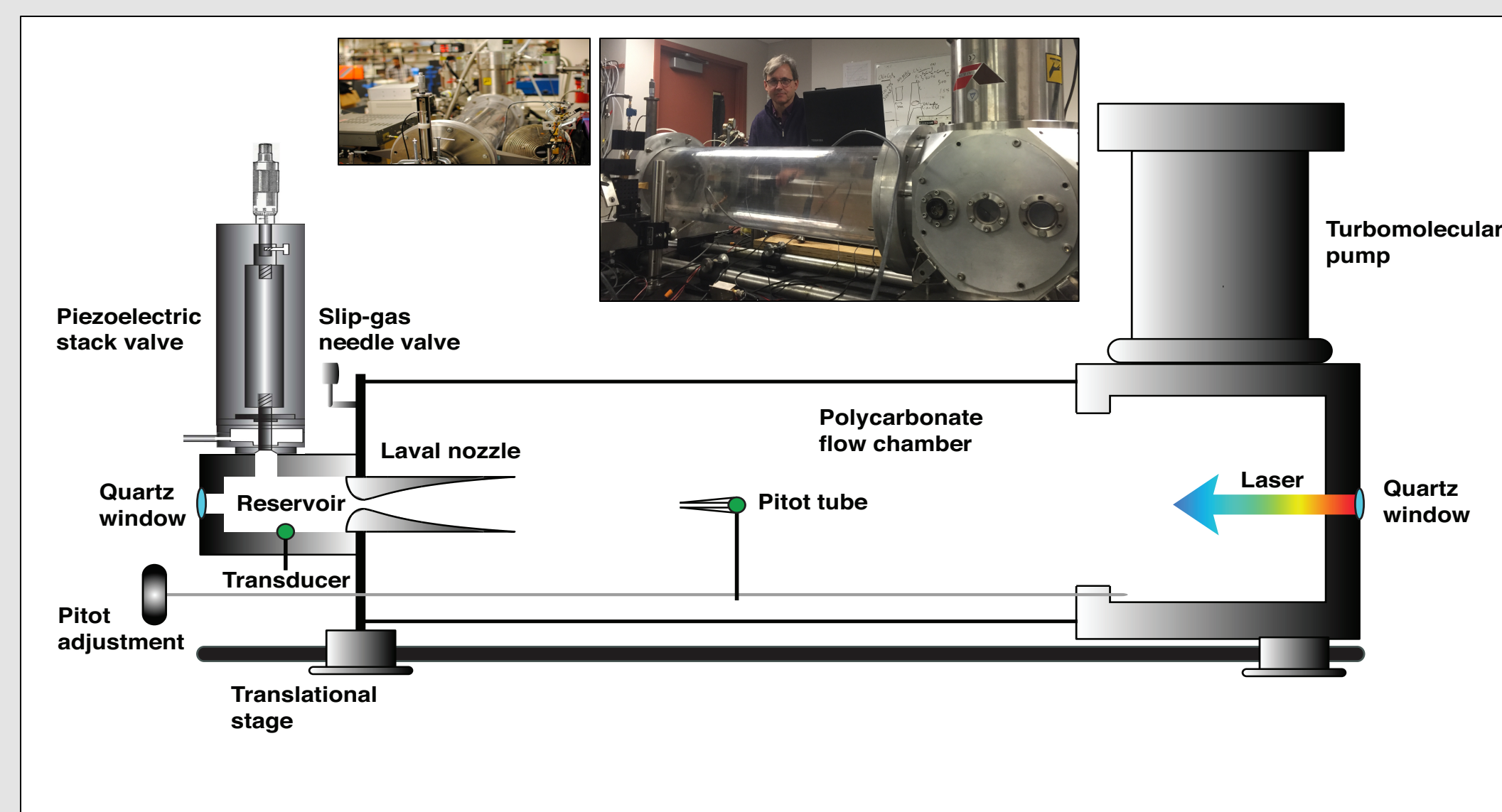
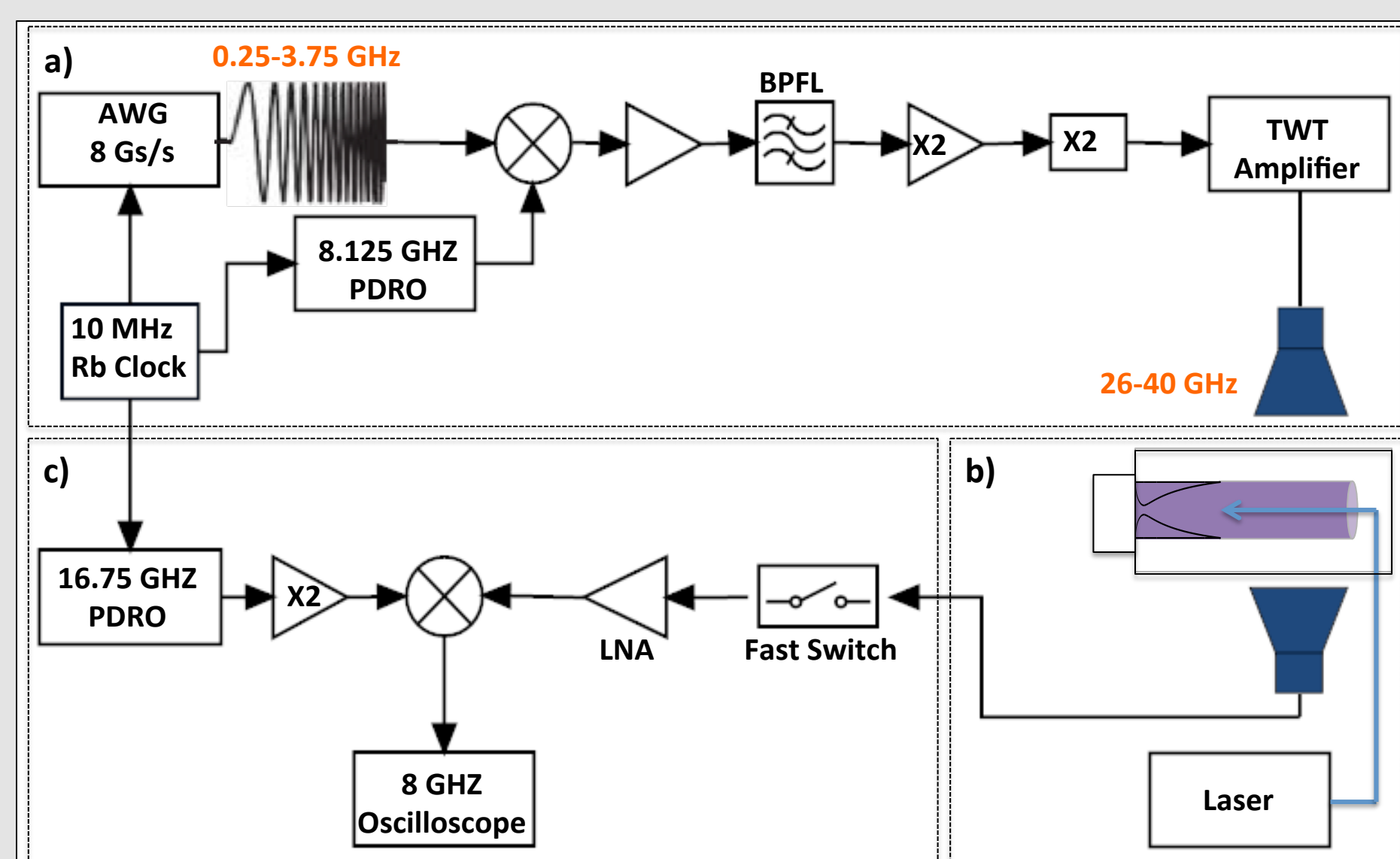
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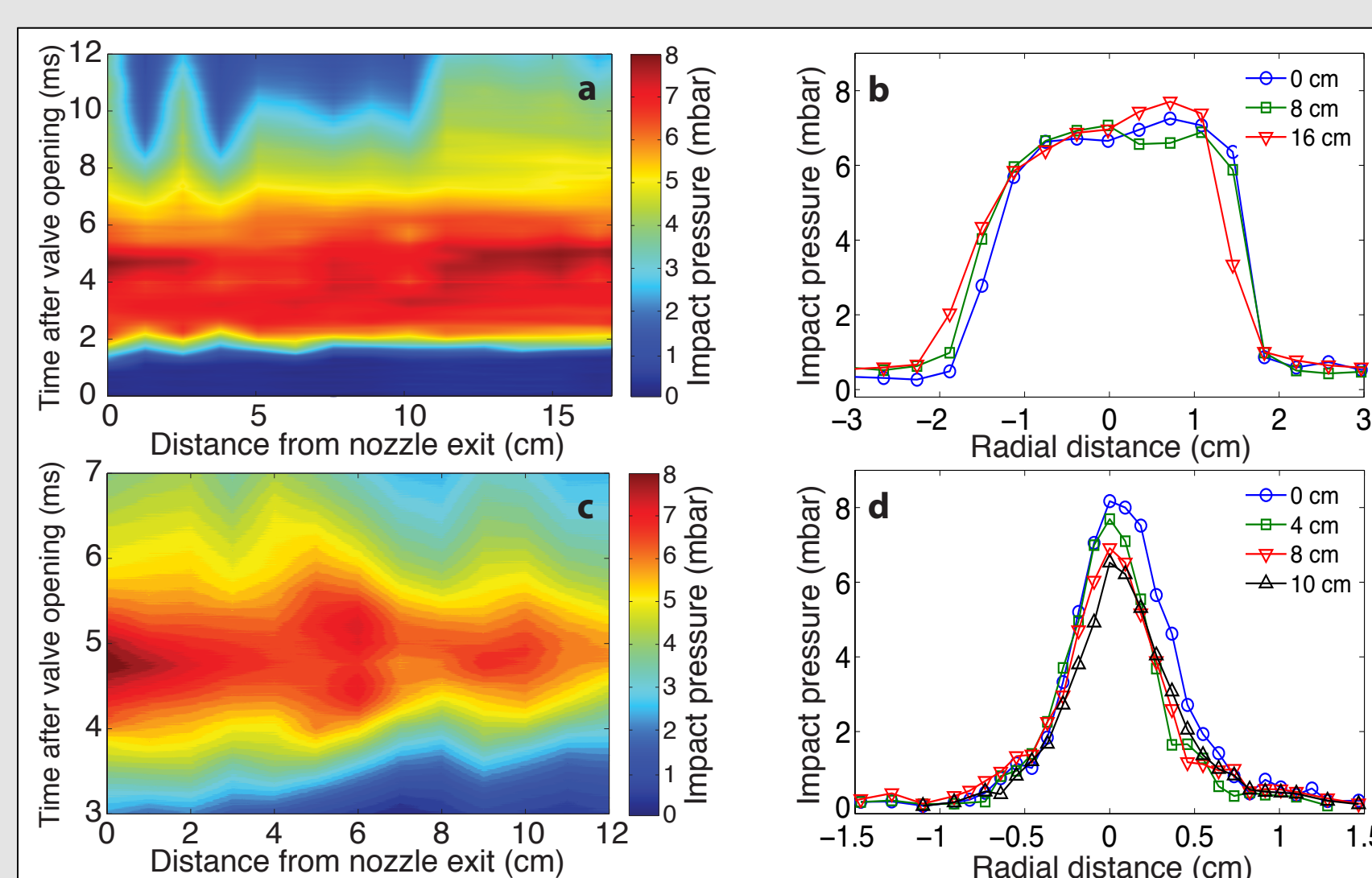
CPUF Spectrometer

A new experimental apparatus is presented that combines two powerful technologies: chirped-pulse Fourier-transform microwave spectroscopy (CP-FTMW) and pulsed uniform supersonic flows to address the need of a detection technique that can give isomer-specific identification and structural characterization of reaction products and intermediates and their branching ratios in the field of reaction dynamics. CP-FTMW spectroscopy is a revolutionary new technique capable of producing broadband rotational spectrum in a single data acquisition. However, a high density (10^{16} cm^{-3}) of cold products (20-30 K) is needed for this approach to be effective. Uniform supersonic flows are an ideal environment for providing these conditions, as well as allowing for stabilization of reaction intermediates and determination of reaction kinetics with product detection. Presented here is a description of the new apparatus, chirped pulse in pulsed uniform supersonic flow (CPUF) spectrometer and its capabilities.



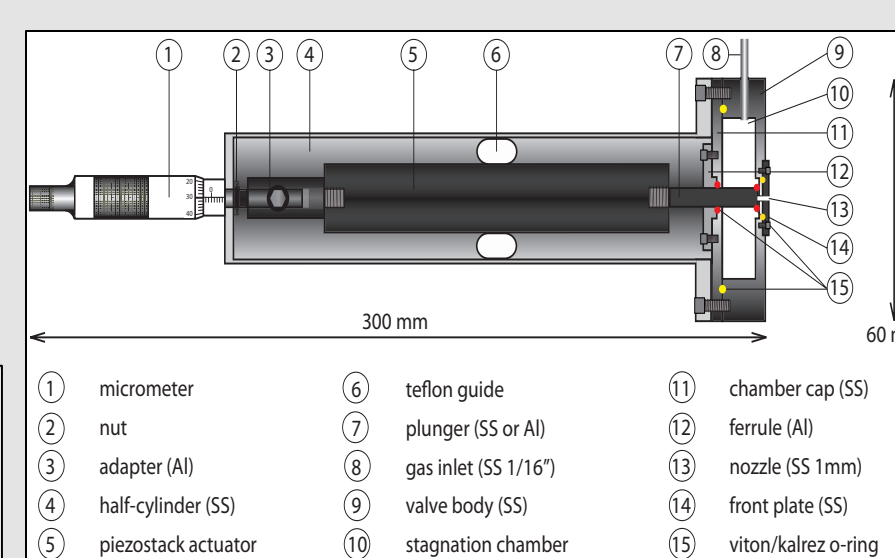
Schematic of the CPUF spectrometer. A chirped pulse is generated in an arbitrary waveform generator (AWG), upconverted, and amplified. The molecular sample is polarized by the radiation and the resulting emission, in the form of a free induction decay (FID), is collected by the oscilloscope. The FID is Fourier transformed to produce a spectrum. The spectrometer operates in the 26-40 and 60-90 GHz frequency regions.

A piezoelectric stack¹ valve is mounted on a small reservoir outside of the polycarbonate vacuum chamber. The Laval nozzle provides a uniform flow with the pressure monitored by a pair of transducers. The entire chamber is mounted on a translational stage, so different regions of the flow can be probed by the microwave radiation introduced via one of the feedhorns.

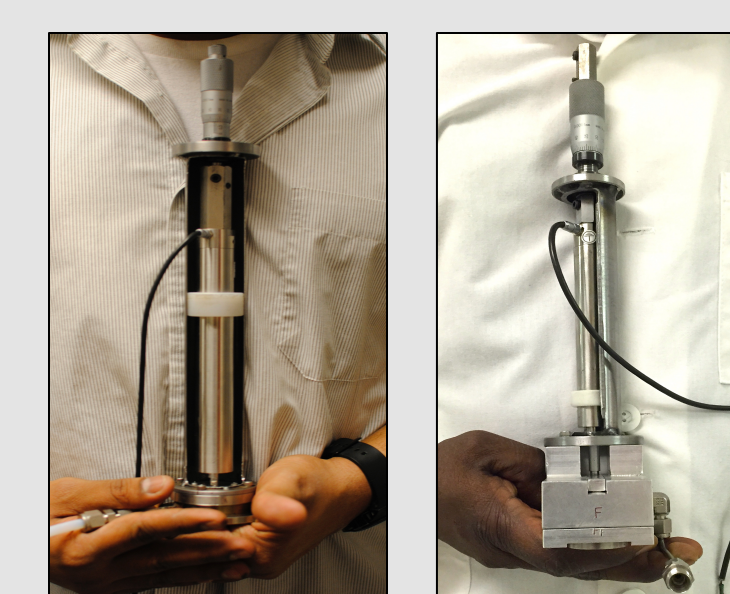


Temperature profiles for the (a) argon and (b) helium Laval nozzles.

Impact pressure measurements and radial profiles for argon (a and b) and helium (c and d), respectively.



Schematic view of the valve assembly.



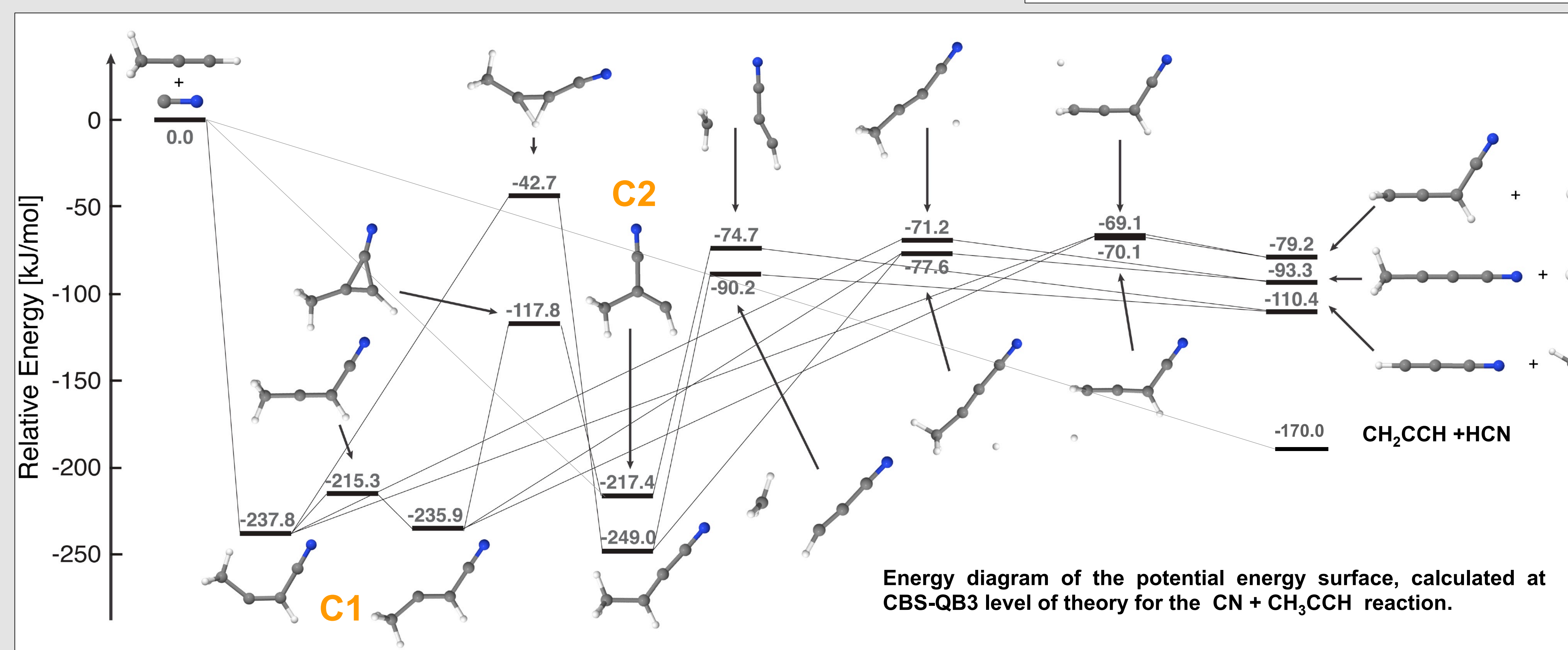
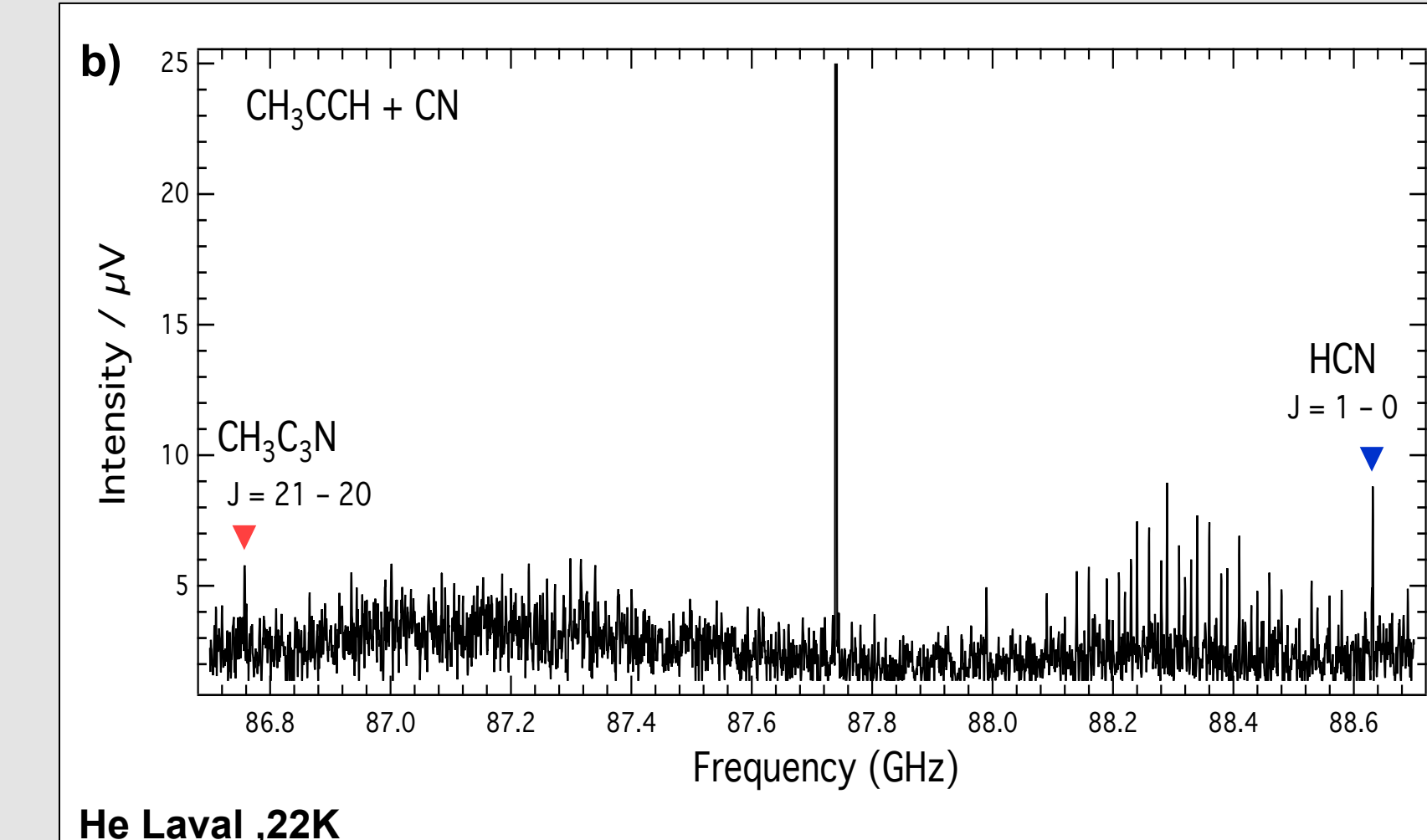
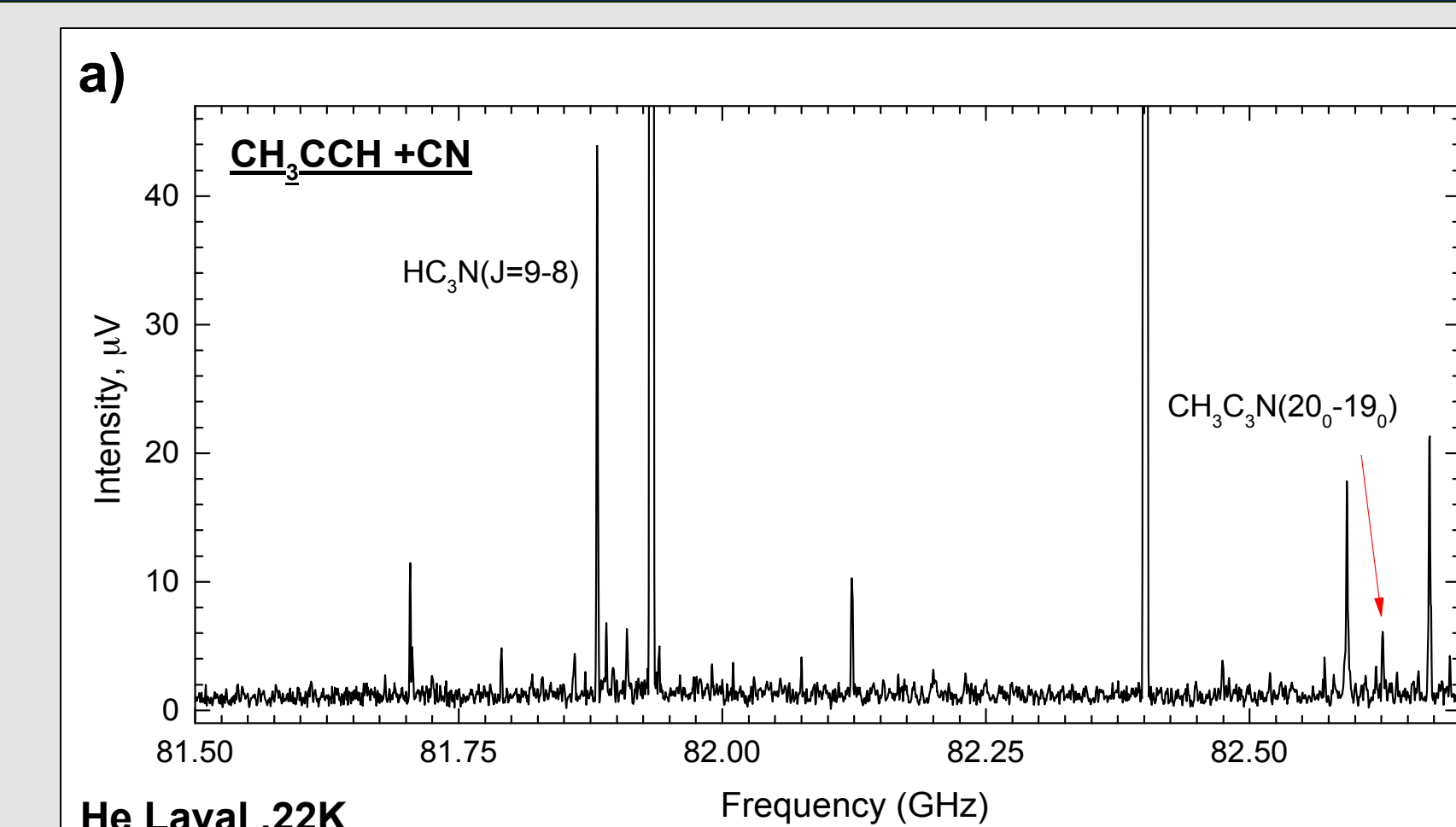
Product branching in the low temperature reaction of CN with Propyne

Motivation

- The reaction between CN radical and methylacetylene (CH_3CCH) is important in the growth of nitrile species in Titan's atmosphere and a prototypical system in the which to probe multichannel branching and the competition between direct and complex-mediated reactions.
- Previous crossed-molecular beam experiments,⁴ supported by ab initio calculations, reported the CN addition/H elimination channel and identified two product isomers.
- Even though CH_3 elimination product HCCCN through C2 is more energetically stable, no clear evidence of this channel was indicated in previous work, nor has the direct abstraction channel been seen previously.

Results & Discussion

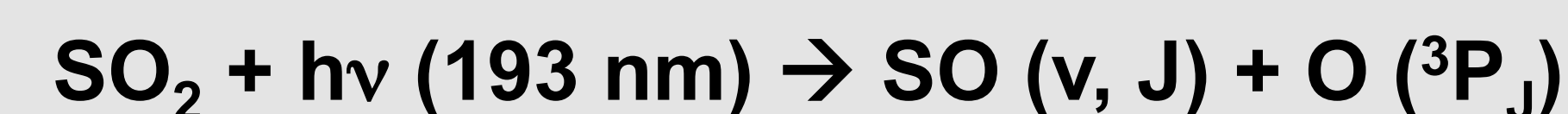
- Both the direct abstraction and the indirect addition/elimination products have rotational transitions accessible within the detection frequency band of CPUF, thus a detailed study of the bimolecular reaction with supporting ab initio calculation was carried out.
- Detection of all the possible products in a broad spectral window allows us to quantitatively determine the product branching ratios for complex bimolecular reactions with multiple product channels.



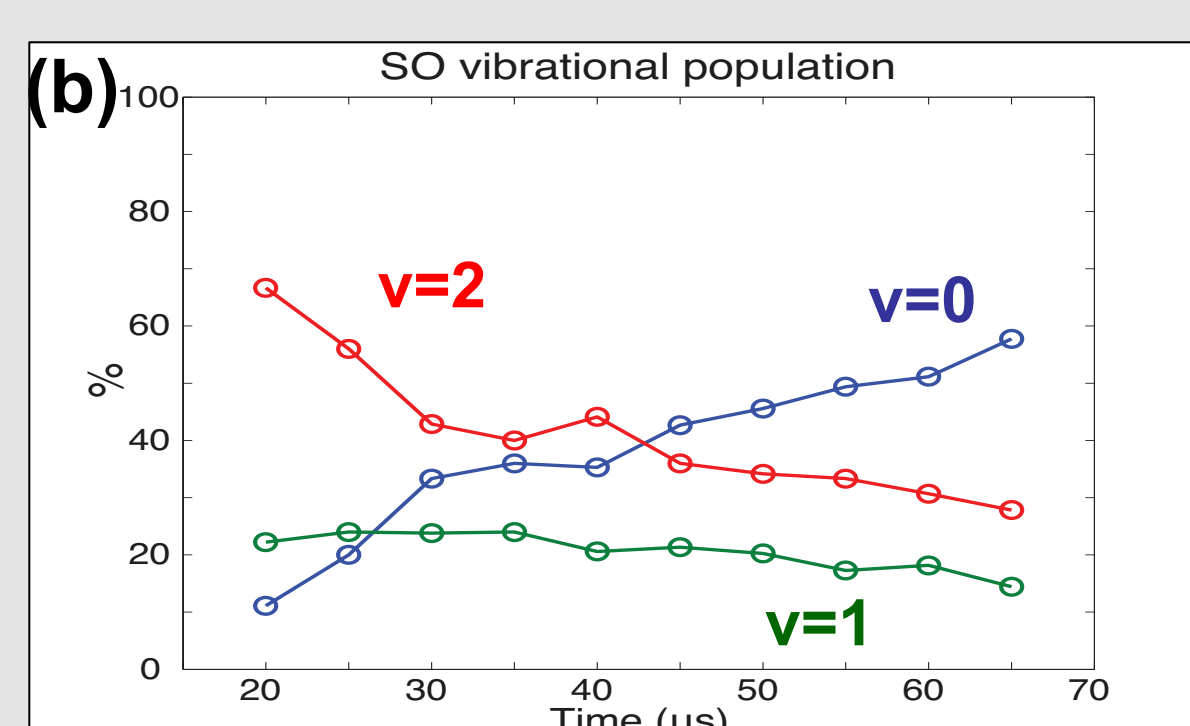
Energy diagram of the potential energy surface, calculated at CBS-QB3 level of theory for the $\text{CN} + \text{CH}_3\text{CCH}$ reaction.

CPUF Capabilities

Photochemistry



Time evolution of SO spectra generated from the photodissociation of SO_2 with 193 nm radiation (a). SO begins to appear roughly 20 μs after the laser is fired, mostly in the $\nu = 2$ vibrational level, corresponding to the nascent vibrational populations determined from imaging studies. However, quick relaxation to the $\nu = 0$ state occurs (b)



Nascent vibrational distributions for $\text{SO} (X^3\Sigma^-)$.

ν	Pop.
0	0.09
1	0.23
2	0.56
3	0.06
4	0.06

Bimolecular Reactions



Spectra illustrating the time evolution of the $J = 4 - 3$ rotational transition of HCCCN ($X^2\Sigma^+$), generated via the bimolecular reaction of the CN radical ($X^2\Sigma^+$) and C_2H_2 ($X^1\Sigma_g^+$), are displayed. The CN radical was produced by irradiation of BrCN with a 193 nm laser. HCCCN appears approximately 40–50 μs after the laser is fired. The inset shows the integrated intensity of the HCCCN line at each time point, with the peak intensity occurring at $\sim 90 \mu\text{s}$. Each spectrum is an average of 22000 acquisitions.

Acknowledgements

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	Addition/elimination			Direct Abstraction	
	%	HC_3N	$\text{CH}_3\text{C}_3\text{N}$	CH_2CCHCN	HCN
RRKM	C1 complex	60	33	7	--
	C2 complex	71	24	5	--
CPUF		72(4)	22(6)	<5	3.5(5)

Calculated and experimental product branching for the CN with CH_3CCH reaction, 2σ uncertainty to the last digit

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