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# A New Experimental Approach to Determine Low-Temperature Product Branching in Multichannel Reactions

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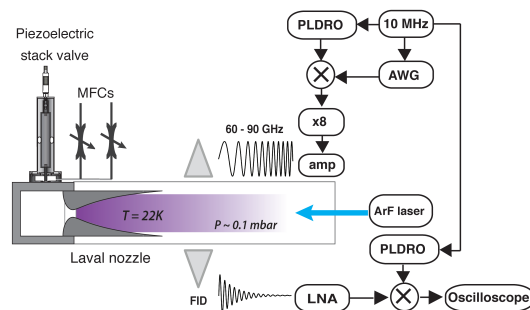
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Nearly all kinetics studies report the observed rate of reactant disappearance, with product identity and branching largely unknown. This limitation arises from considerable experimental challenges inherent in the quantitative detection of the full range of products of a given reaction, particularly for large polyatomic systems. Recent advances have relied upon tunable synchrotron photoionization or low-energy electron impact ionization to achieve selective product detection in dynamics, kinetics, and flame studies. Challenges remain, however, as these studies require fitting of composite and often incompletely resolved spectra to infer branching, and clear product signatures are often lacking. To address these issues, we have developed an alternative approach, which incorporates chirped-pulse Fourier transform microwave spectroscopy [1] in low-temperature uniform supersonic flows [2] ("chirped-pulse / uniform flow", C-PUF). This technique provides clear quantifiable spectroscopy signatures of polyatomic products in bimolecular or unimolecular reactions for virtually any species with a modest electric dipole moment.

## Chirped-Pulse / Uniform Flow

### Schematic

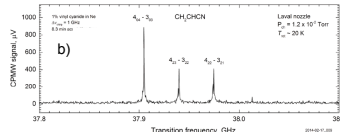
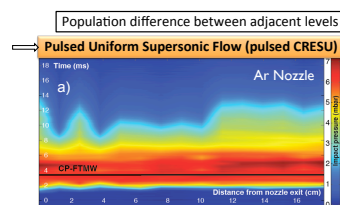
- Flow Chamber:** The pulsed uniform flow source consists of a piezoelectric stack valve connected to mass flow controllers (MFC), and a Laval nozzle mounted on one end of a polycarbonate vacuum chamber. A quartz window is located on the other end of the chamber to allow radiation from an ArF excimer laser to propagate down the axis of the Laval nozzle, such that the core of the flow is irradiated.
- Spectroscopy CP-FTMW:** Linearly chirped pulses (0.25–3.75 GHz) are produced in an arbitrary waveform generator (AWG) and then mixed with a local oscillator (frequency 8.125 GHz) phase-locked to a 10 MHz Rb clock. Frequencies are then multiplied, amplified, and broadcast onto the flow via a feedhorn oriented perpendicular to the flow axis. Bandpass filters and isolators are inserted into the setup as necessary. The resultant molecular emission, a free induction decay (FID) is collected by a second feedhorn, amplified through a low noise amplifier (LNA), downconverted before detection, and phase-coherently averaged in a broadband fast oscilloscope (8 GHz, 25 Gs/s), where it is Fourier transformed to produce a pure rotational spectrum with MHz resolution.



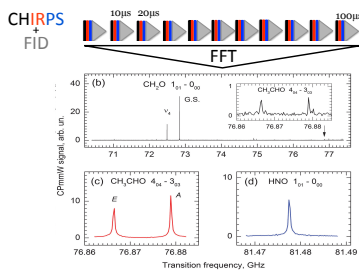
$$S \propto \omega \mu^2 E_{\text{pulse}} \Delta N_0 \sqrt{\frac{\pi}{\alpha}}$$

Linear sweep rate  
 Segmented chirps

### How to maximize signal?

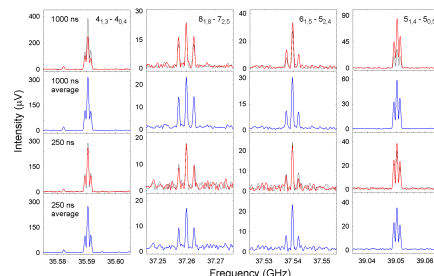


(a) The impact pressure profile from an Ar Laval nozzle from which a temperature of 22 K is derived.  
 (b) CP-FTMW rotational spectrum of vinyl cyanide CH<sub>2</sub>CHCN showing a temperature of ~20 K. Ref. [4]



Typical time sequence with segmented chirps to monitor the products formed in the pyrolysis of CH<sub>3</sub>CH<sub>2</sub>ONO. Here a broadband 7 GHz chirp covering 70.4–77.4 GHz (black) is used in combination with 20 MHz chirps centered on relevant known transitions for CH<sub>3</sub>CHO (red) and HNO (blue). Ref. [3]

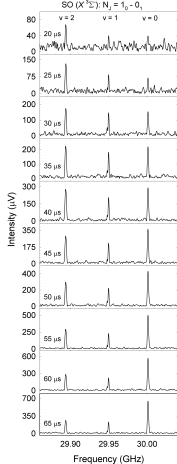
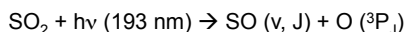
### On the collisional environment



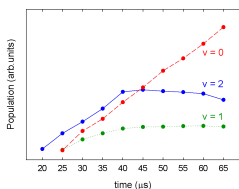
Several rotational transitions of dimethyl ether (J<sub>K<sub>a</sub>,K<sub>c</sub></sub> - J<sub>K<sub>a</sub>,K<sub>c</sub>'</sub>) over the 34–40 GHz frequency range are shown to illustrate the effects of collisional dephasing on signal intensities. The top row of spectra was taken with chirp duration of 1000 ns, and a clear asymmetry exists in the line intensities between up- (red trace) or down-swept (black) frequencies. This asymmetry is less severe in spectra obtained with a 250 ns chirp duration (middle row) or shorter. Averaging up- and down-chirped spectra can compensate for the dephasing effects, as shown in rows two and four (blue traces) for the 1000 and 250 ns spectra, respectively. Ref. [5]

## Applications for reaction dynamics and astrochemistry

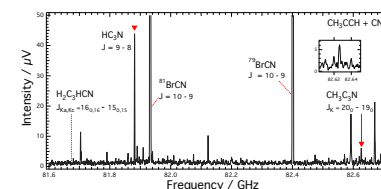
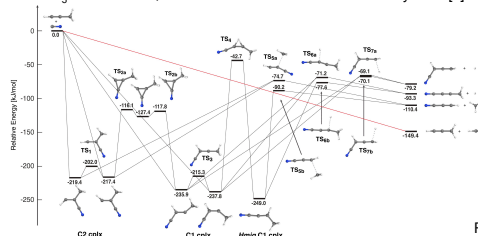
### Photodissociation of SO<sub>2</sub>



Time evolution of SO spectra generated from the photodissociation of SO<sub>2</sub> with 193 nm radiation. SO begins to appear 20 μs after the laser is fired at 65% in the ν = 2 vibrational level. This value is in good agreement with the nascent vibrational populations determined from imaging studies. Ref. [5]



Key stationary points on the potential energy surface for the CN + CH<sub>3</sub>CCH reaction, calculated at CBS-QB3 level of theory. Ref. [6]



### Product Branching for CN + C<sub>2</sub>H<sub>4</sub>

Product branching, in percent, at 22 K with 2σ uncertainty in the last digit.

	addition-elimination			direct abstraction
	HCCCN	CH <sub>3</sub> CCHN	CH <sub>3</sub> CCN	HCN
CPUF	66(4)	22(6)	0(8)	12(5)
RRKM	C1 cplx: 48	33	7	
	C2 cplx: 65	19	4	

Relative product populations is deduced from the spectra using the relationship between the integrated line intensities (W) and column densities (N<sub>tot</sub>):

$$W = \frac{4\pi^{3/2} \omega_0^2 S_{\mu}^2 g_{\text{gK}} \epsilon}{c \sqrt{\alpha}} \frac{N_{\text{tot}}}{k_{\text{rot}} Q_{\text{rot}}} e^{-E_i/kT_{\text{rot}}}$$

Segmented macrochirp scan that targets transitions of HCCCN, CH<sub>3</sub>CCHN, and CH<sub>3</sub>CCN: J = 9–8 transition at 81.881 GHz, J<sub>K<sub>a</sub>,K<sub>c</sub></sub> = 16<sub>0,16</sub> – 15<sub>1,15</sub> at 81.674 GHz and J<sub>K</sub> = 200 – 190 at 82.627 GHz. The inset shows the K = 0, 1, 2, and 3 transitions of CH<sub>3</sub>CCN. Ref. [6]

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