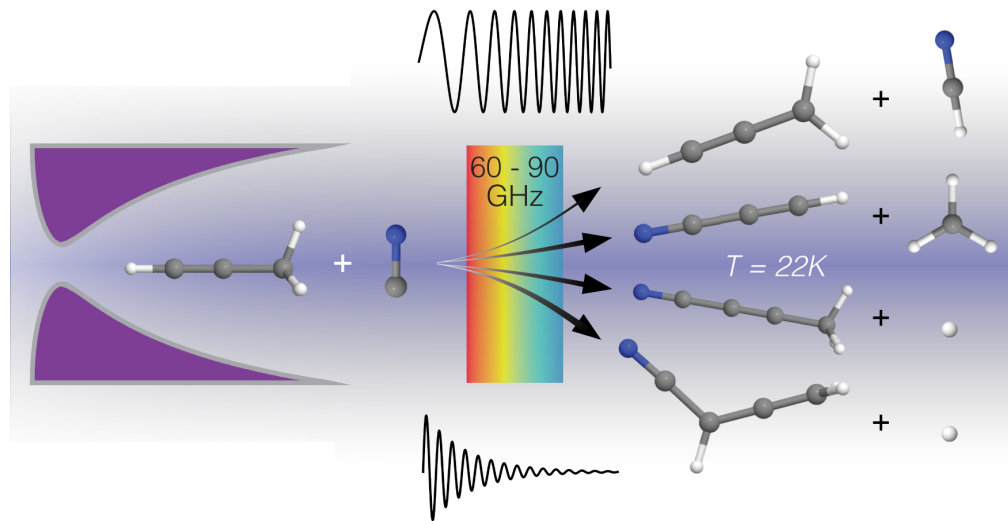


# CHIRPED-PULSE IN UNIFORM FLOW

Baptiste Joalland

Chamara Abeysekera, Lindsay N. Zack, Nuwandi M. Ariyasingha  
Ian R. Sims, Robert W. Field, Arthur G. Suits



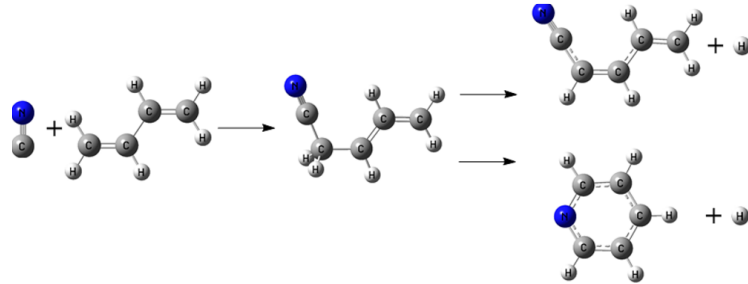
WAYNE STATE  
UNIVERSITY



Massachusetts  
Institute of  
Technology

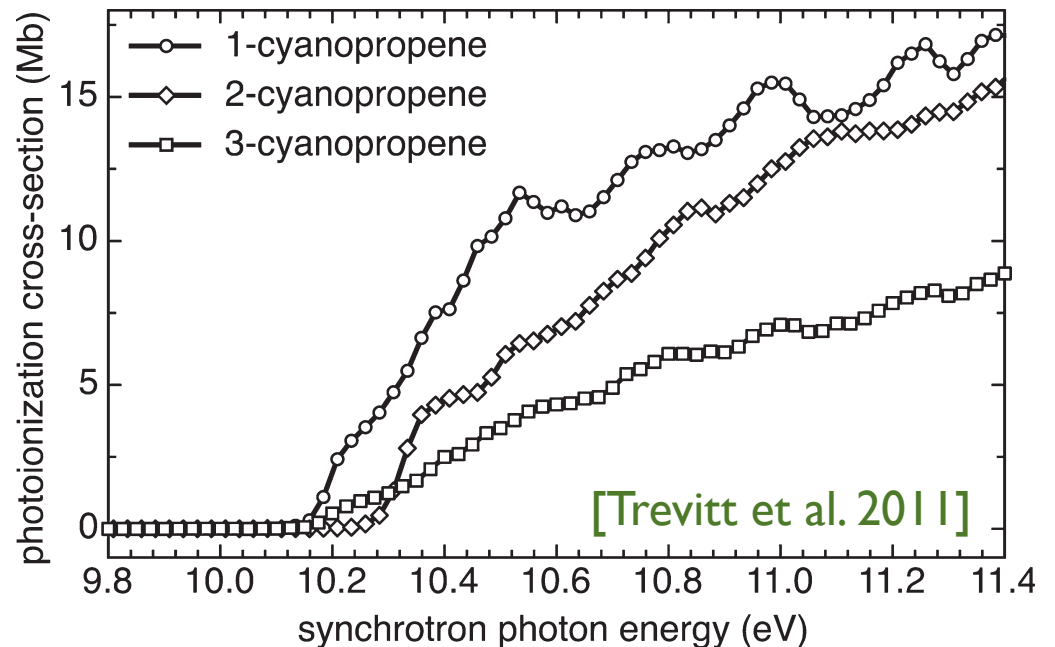
# Current Challenges for Laboratory Astrophysics

## How to Determine Reaction Rates and Low-Temperature Branching Ratios?



Nearly all kinetics studies report the observed rate of *reactant disappearance*, with product identity and branching largely unknown.

Recent advances have relied upon tunable VUV from synchrotron sources. However, these studies require complex fitting to infer branching, and clear product signatures are often lacking.



# A New Approach

## **Chirped-Pulse MicroWave Spectroscopy**

developed by Brooks Pate and migrated to higher frequencies by R.W. Field and coworkers

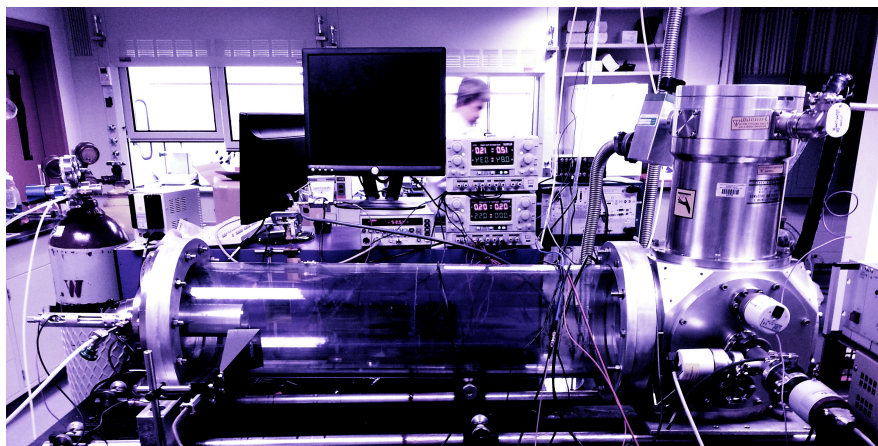
[G. G. Brown *et al*, 2008]

*combined with*

## **Pulsed Uniform Supersonic Flows**

thermalized flows at  $\sim 20$  K and high density via Laval nozzle, developed by B.R. Rowe, I.W.M. Smith, and I.R. Sims - CRESU

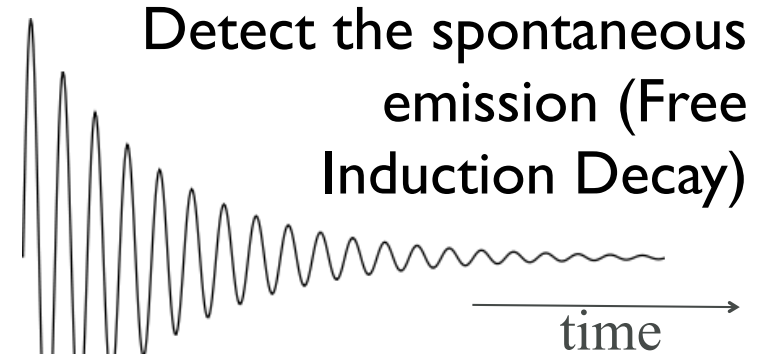
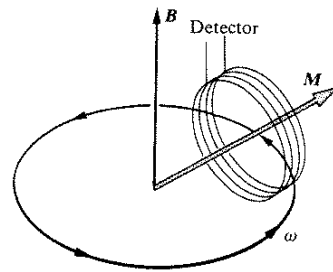
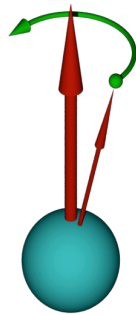
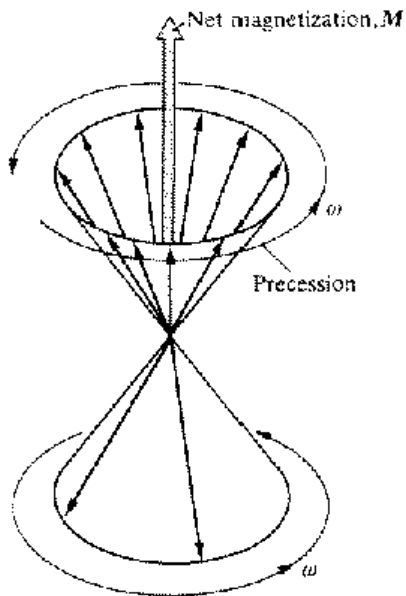
[I. R. Sims *et al*, 1994]



**Rotational spectroscopy becomes a tool for  
Kinetics/Dynamics and Astrochemistry**

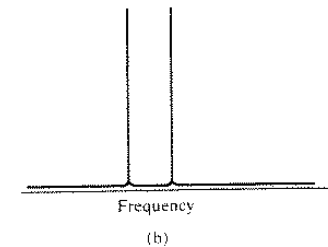
# Chirped-Pulse Microwave Spectroscopy

*Analogy with NMR*



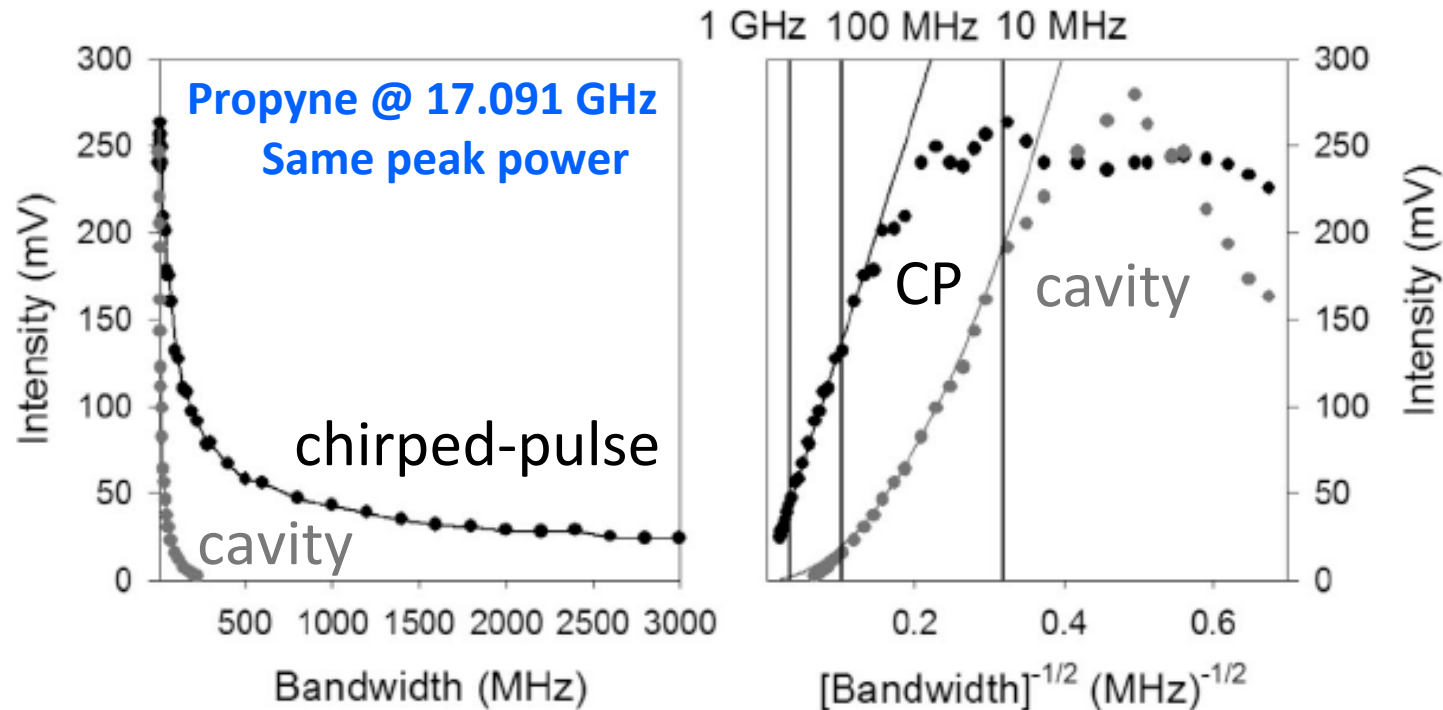
Apply RF  $\mathbf{B}$  field

Fourier transform to obtain the spectrum



# Chirped-Pulse Microwave Spectroscopy

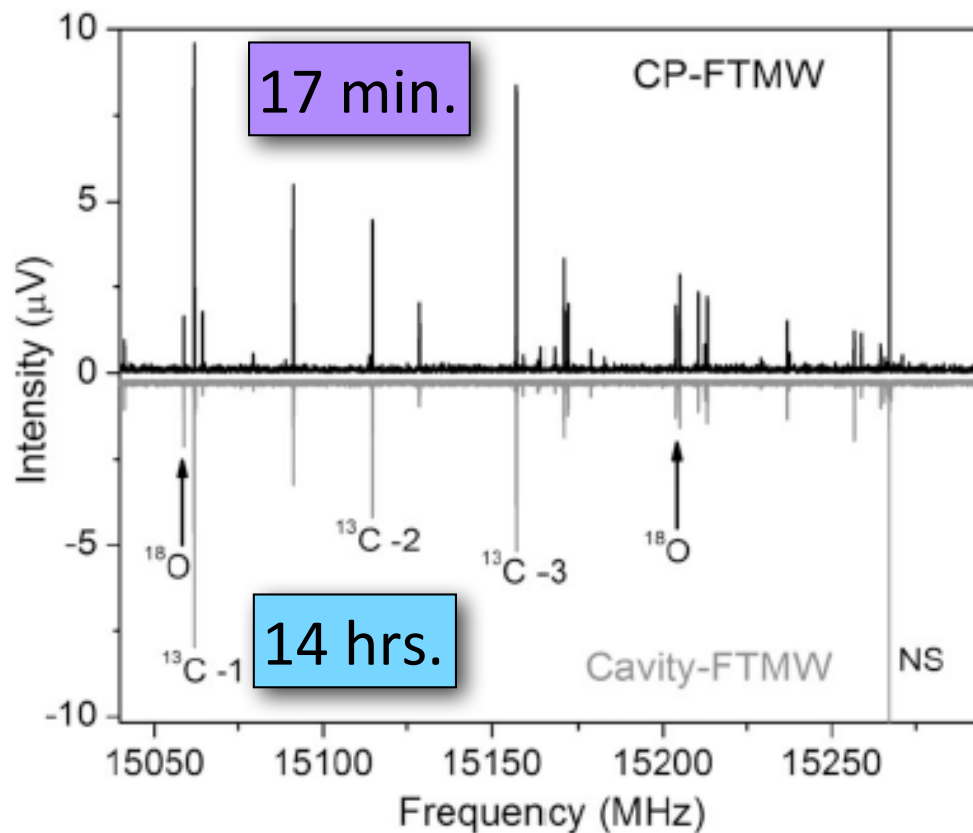
*What is so special about it?*



- ★ No need to step cavity dimension
- ★ Pulse duration and power are independent
- ★ Signal scales as  $(\text{bandwidth})^{-1/2}$

# Chirped-Pulse Microwave Spectroscopy

*What is so special about it?*



This suggests broadband rotational spectroscopy could be used, like REMPI or LIF or VUV, as a very general probe of reaction dynamics, with detailed structural information at the same time.

# Chirped-Pulse Microwave Spectroscopy

Chirped pulse generated by arbitrary waveform generator and upconverted to desired region

Broadband excitation (several GHz) possible in a few ns

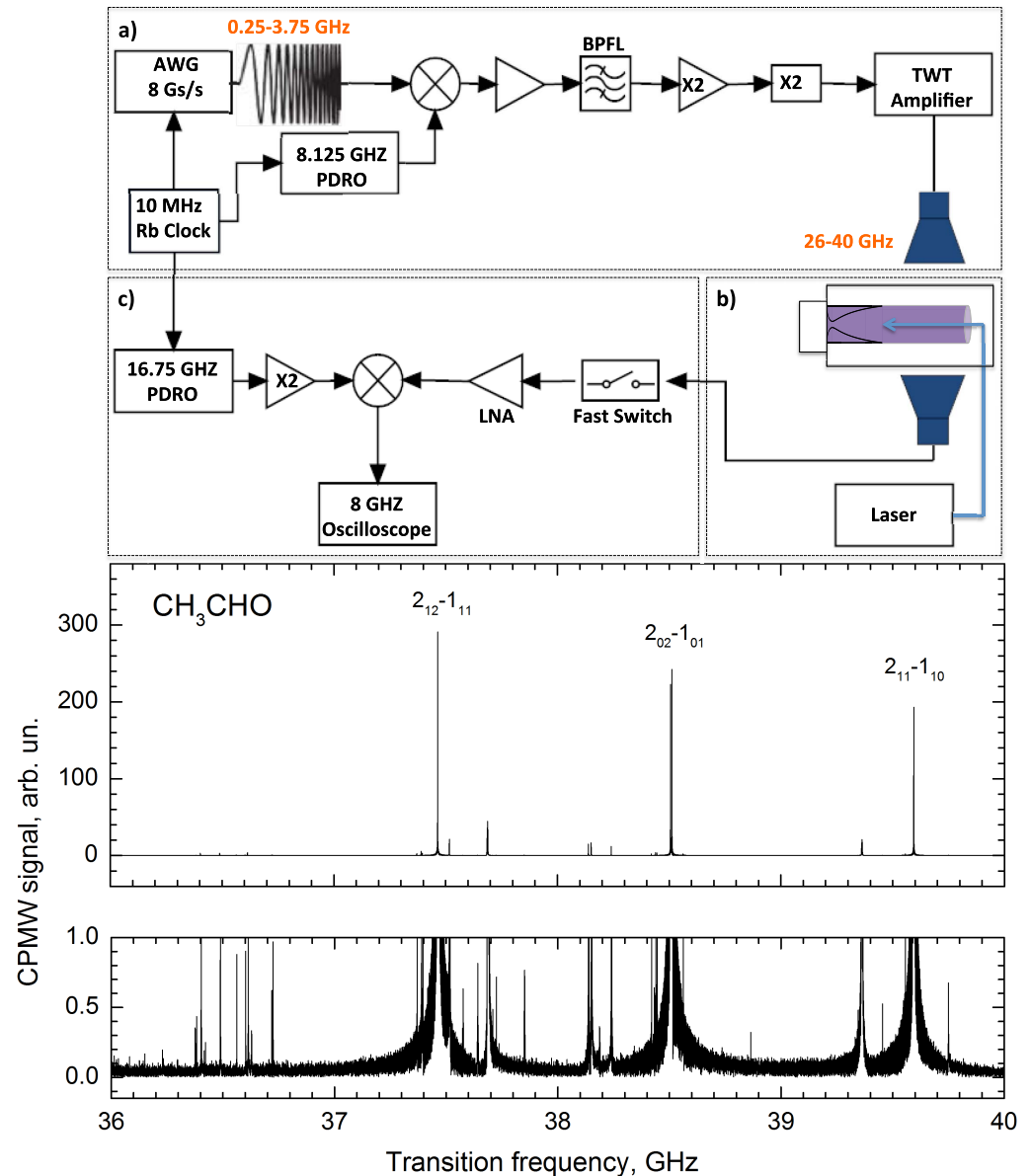
Low frequency system ( $K_a$  band):

- ★ 26-40 GHz
- ★ peak power 40 W

High frequency system (W band)

- ★ 60-90 GHz
- ★ peak power 100 mW

Collaboration with Field group @ MIT



# Chirped-Pulse Microwave Spectroscopy

How do we maximize signal?

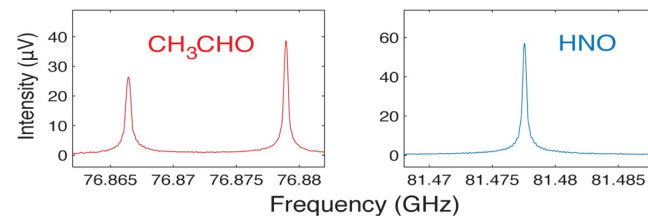
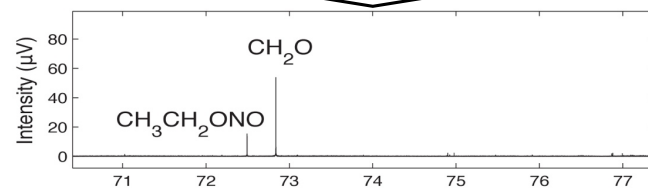
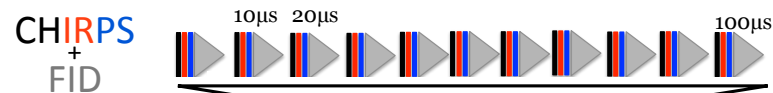
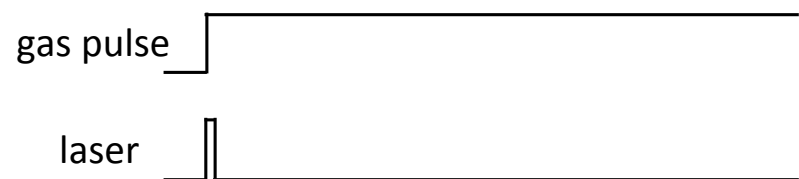
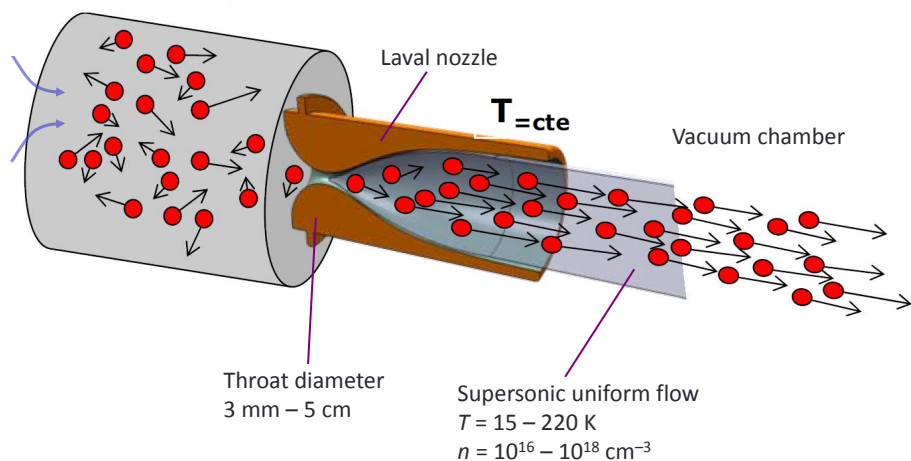
$$S \propto \omega \mu^2 E_{pulse} \Delta N_0 \sqrt{\frac{\pi}{\alpha}}$$

← Linear sweep rate

Population difference  
between adjacent levels

=> *CRESU*

=> *segmented chirps*



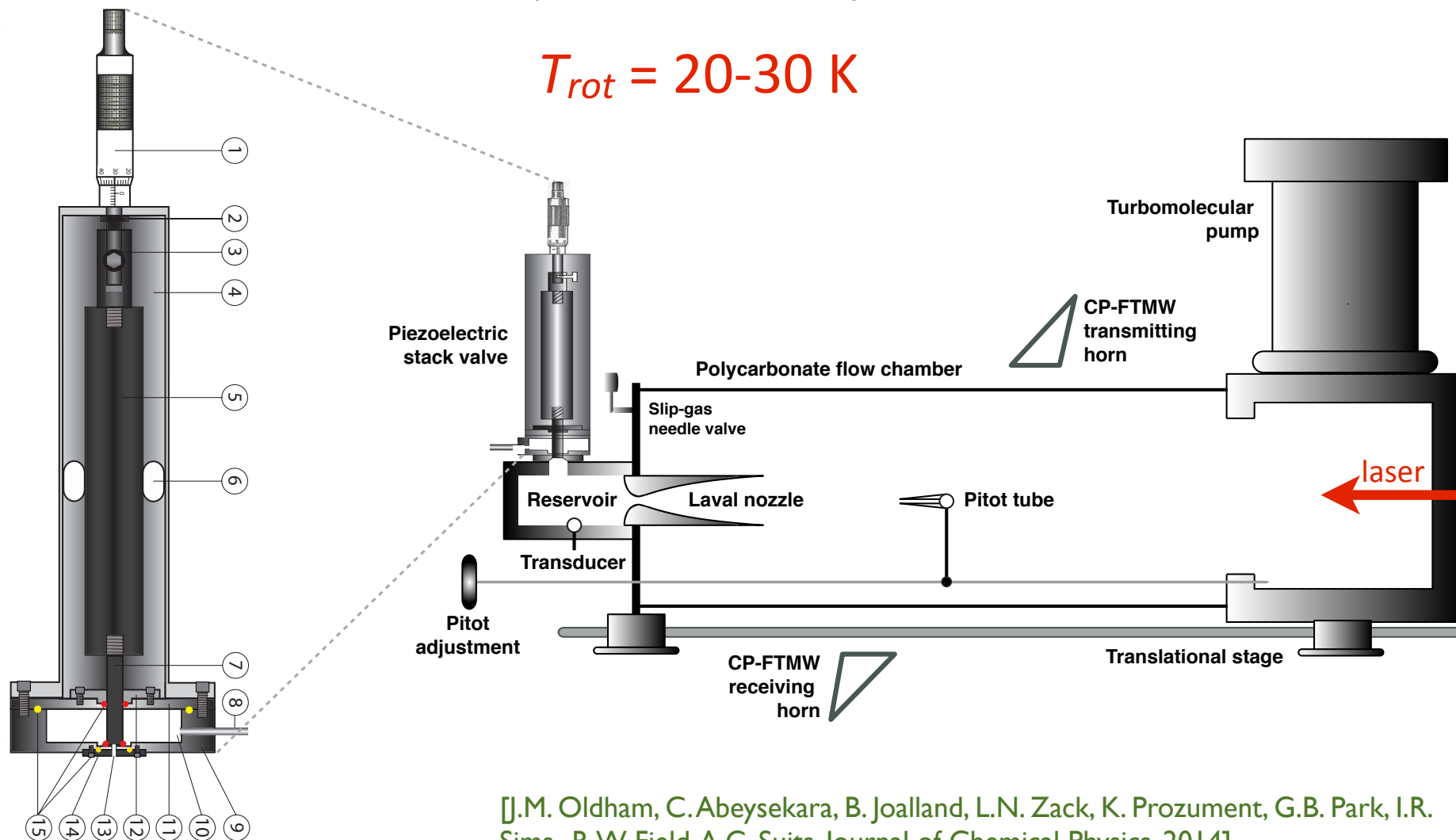
Collaboration with I.R. Sims @ IPR



# Pulsed Uniform Supersonic Flow

(Pulsed CRESU)

$$T_{rot} = 20-30 \text{ K}$$

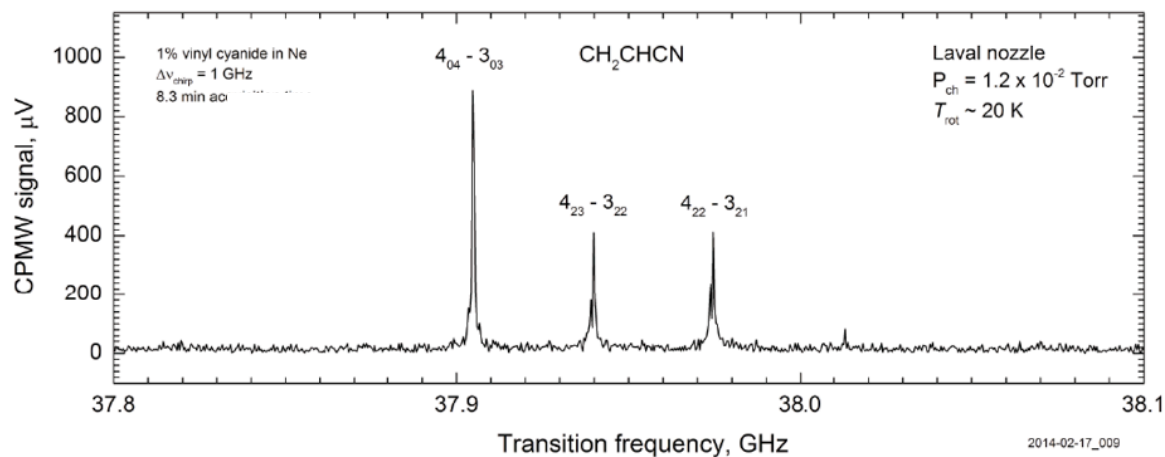
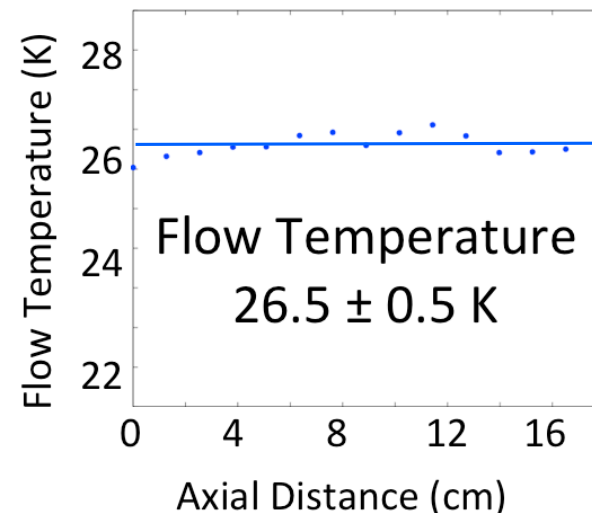
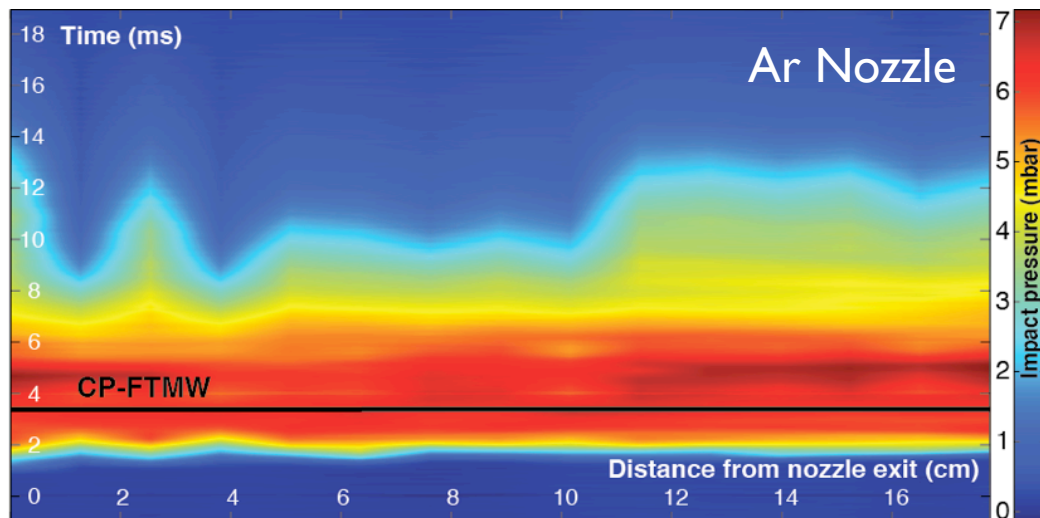


[J.M. Oldham, C. Abeysekara, B. Joalland, L.N. Zack, K. Prozument, G.B. Park, I.R. Sims., R.W. Field, A.G. Suits, *Journal of Chemical Physics*, 2014]

[C. Abeysekara, L.N. Zack, G.B. Park, B. Joalland, J.M. Oldham, K. Prozument, N.M. Ariyasingha, I.R. Sims., R.W. Field, A.G. Suits, *Journal of Chemical Physics*, 2014]

# Chirped-Pulse in Uniform Flow

## Pulsed Uniform Supersonic Flow (Pulsed CRESU)



Excellent agreement  
between flow temperature  
and rotational temperature

[C. Abeysekara, L.N. Zack, G.B. Park, B. Joalland, J.M. Oldham, K. Prozument, N.M. Ariyasingha, I.R. Sims., R.W. Field, A.G. Suits, *Journal of Chemical Physics*, 2014]

# Chirped-Pulse in Uniform Flow

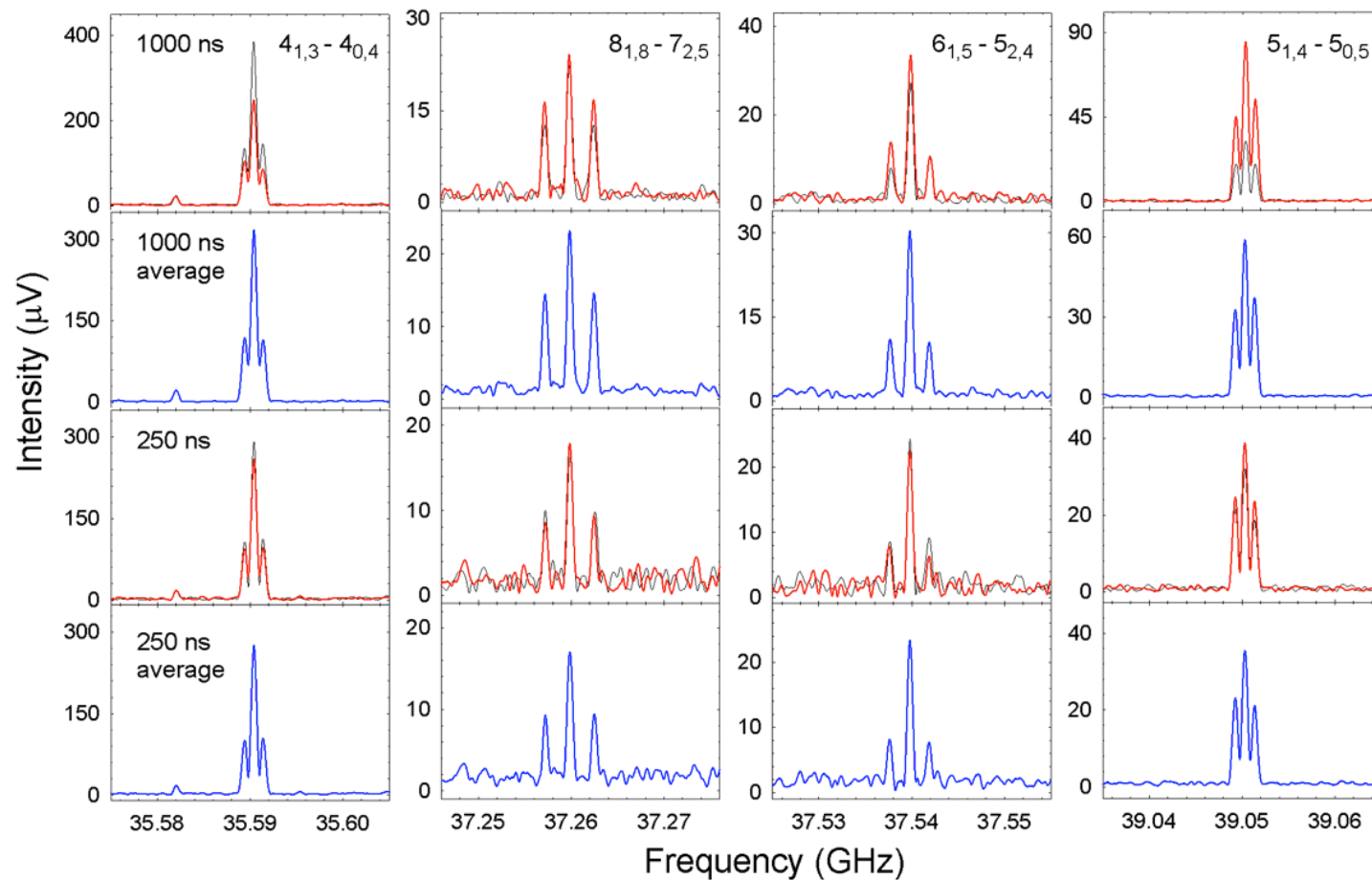
*On the (High) Collisional Environment*

dimethyl-ether  $\text{CH}_3\text{OCH}_3$

mean free path  $\sim 30 \mu\text{m}$  ; mean time  $90 \text{ ns}$

up  
down

up  
down



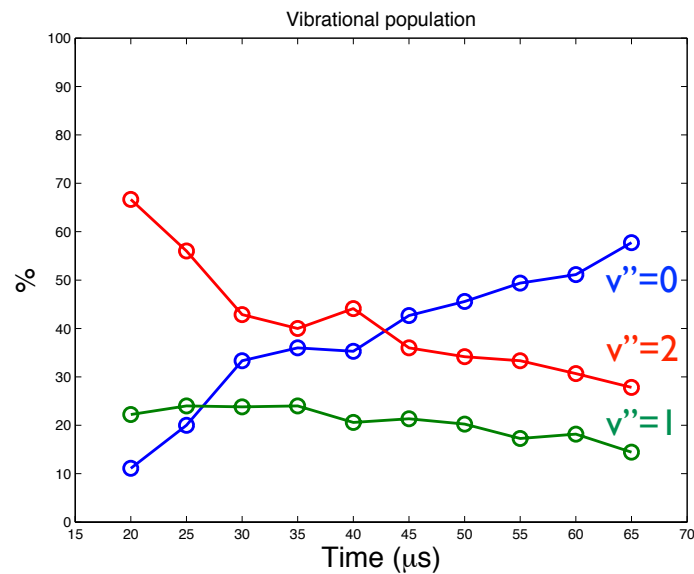
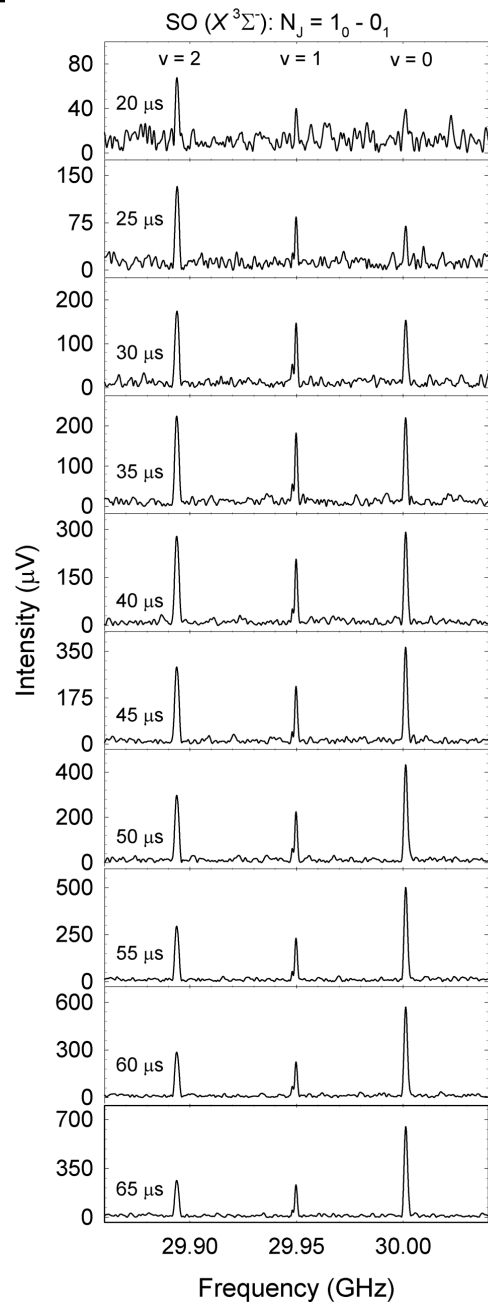
$\Rightarrow$  the coherence time is shortened by dephasing phenomena

# Chirped-Pulse in Uniform Flows

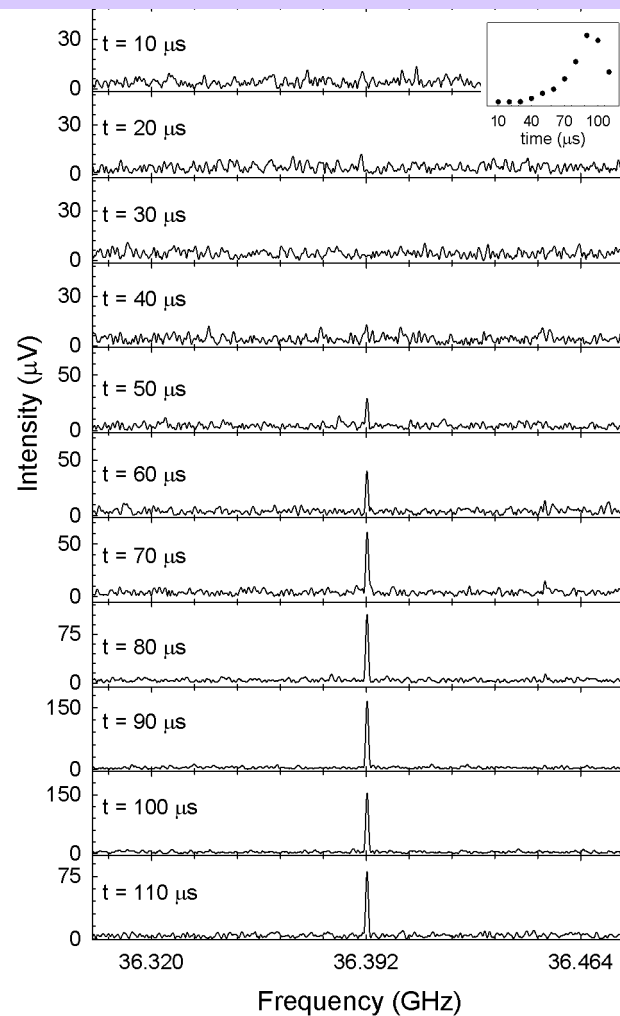
## Applications for Reaction Dynamics

Photodissociation of  $\text{SO}_2$  at 193nm:  
Probing the nascent vibrational  $\text{SO} (X^3\Sigma^-)$

Reaction of  $\text{CN} + \text{C}_2\text{H}_2$  at 20K:  
Probing  $\text{HC}_3\text{N}$



$v''$	Population (%)			
	REMPI + VMI <sup>a</sup>	LIF <sup>b</sup>	IR <sup>c</sup>	CPUF <sup>d</sup>
0	9	2	...	20
1	23	20	20	21
2	56	83	70	58
3	6	0	...	...
4	6	...	...	...
5	...	...	<10	...

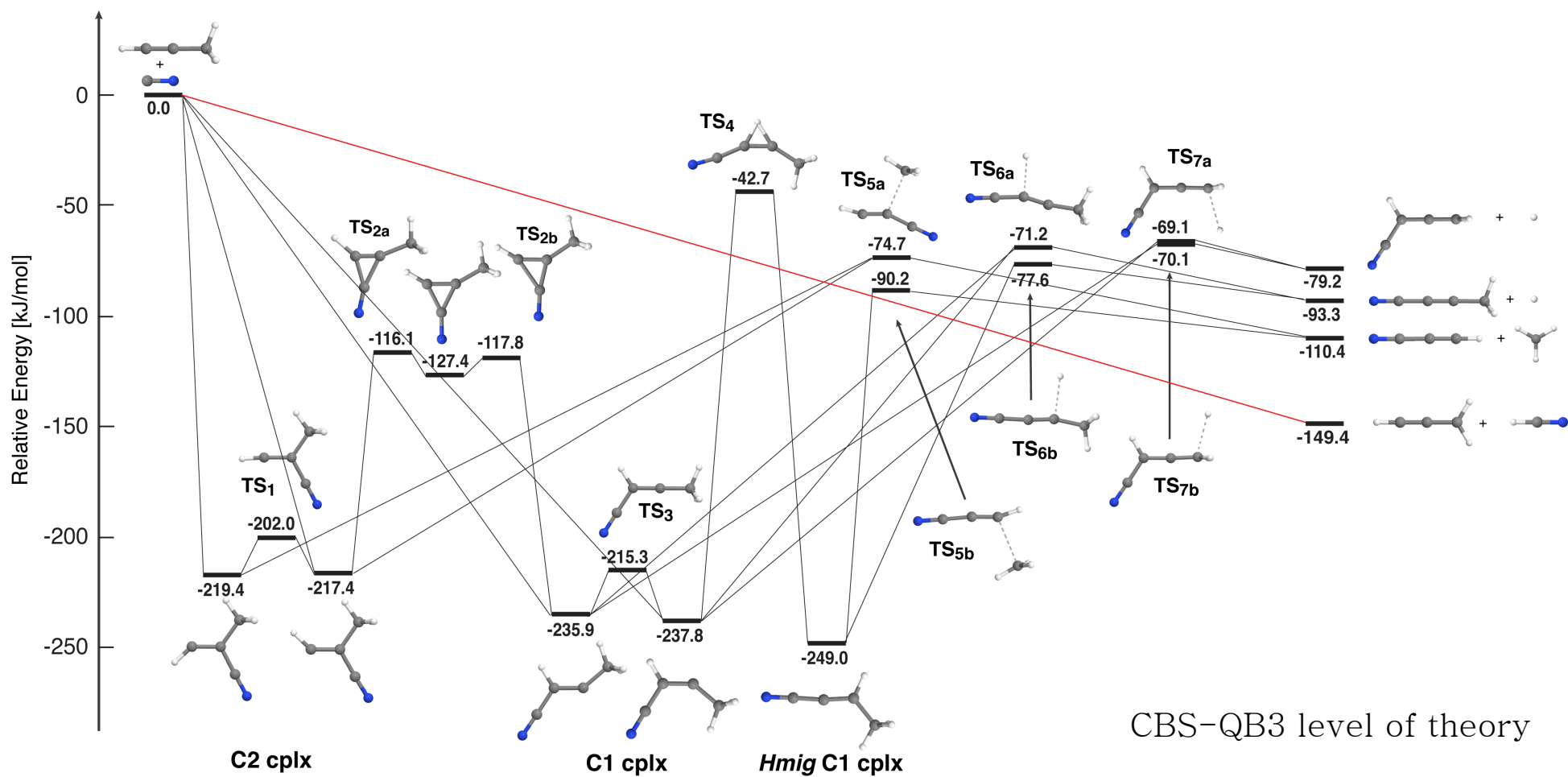


[C. Abeysekera, L.N. Zack, G.B. Park, B. Joalland, J.M. Oldham, K. Prozument, N.M. Ariyasingha, I.R. Sims., R.W. Field, A.G. Suits, *Journal of Chemical Physics*, 2014]

# Chirped-Pulse in Uniform Flow

## Applications for Multichannel Reactions

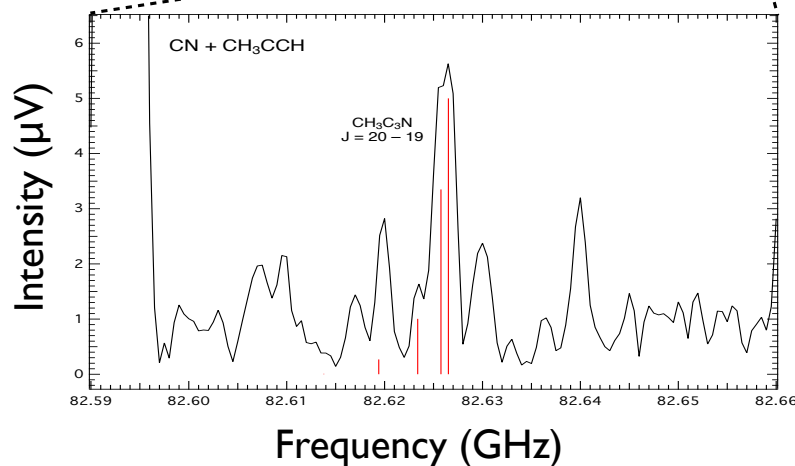
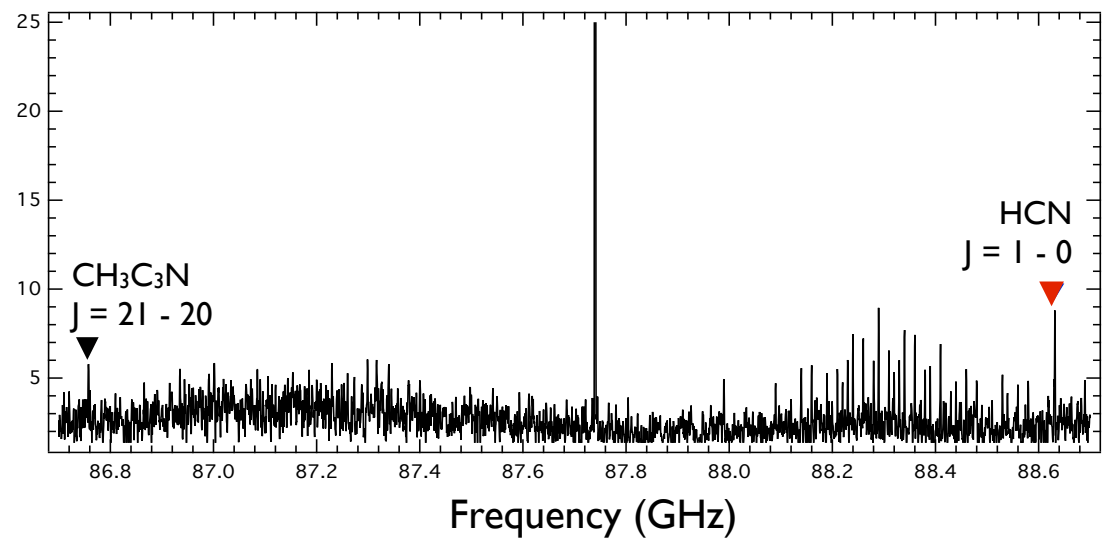
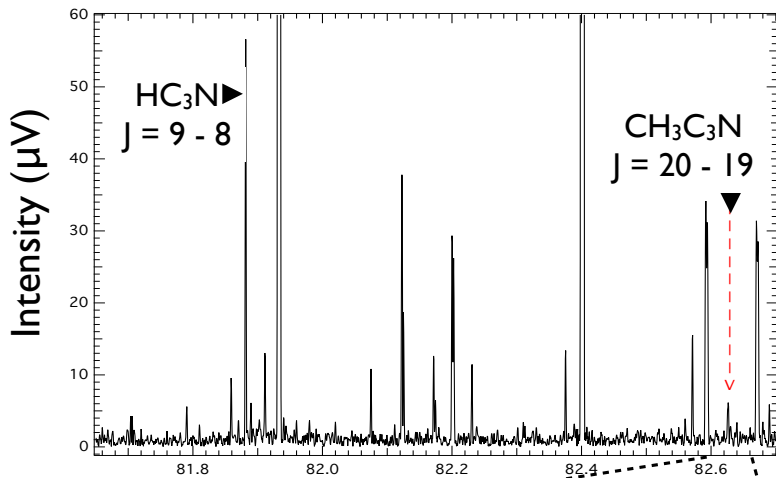
CN + propyne ( $C_3H_4$ ) @ 22K



# Chirped-Pulse in Uniform Flow

## Applications for Multichannel Reactions

CN + propyne ( $C_3H_4$ ) @ 22K



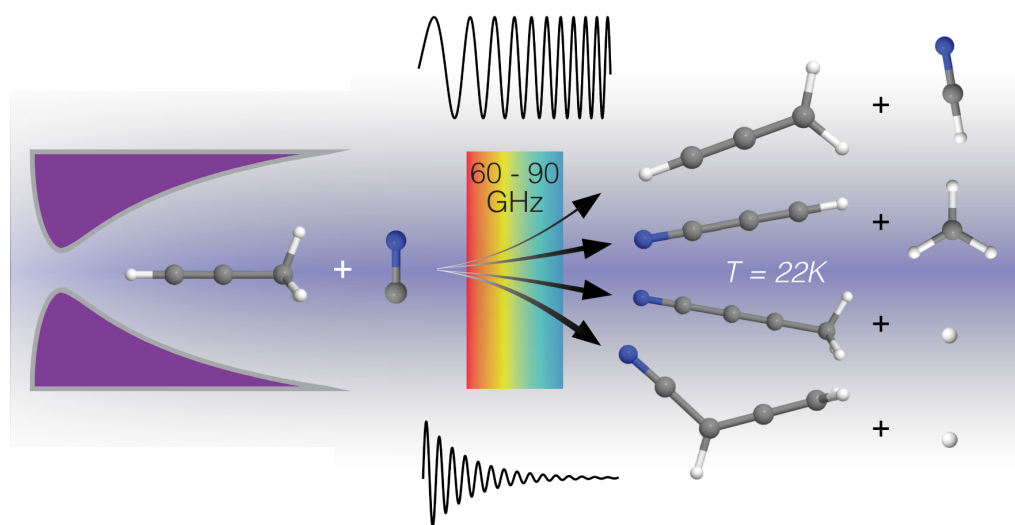
Integrated line intensity:

$$W = \frac{4\pi^{3/2} \omega_0^2 S \mu_i^2 g_l g_I \epsilon}{c \sqrt{\alpha}} \frac{N_{tot}}{kT Q_{rot}} e^{-E_l/kT_{rot}}$$

# Chirped-Pulse in Uniform Flow

## Applications for Multichannel Reactions

CN + propyne ( $C_3H_4$ ) @ 22K



branching (%):

<u>CPUF</u>	<u>CI</u>	<u>RRKM</u>	<u>C2</u>
12(5)	-	-	-
66(4)	48		65
22(6)	33		19
0(8)	7		4

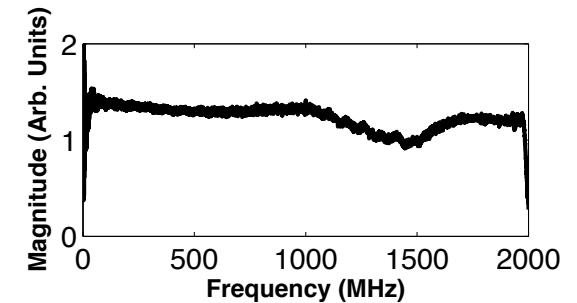
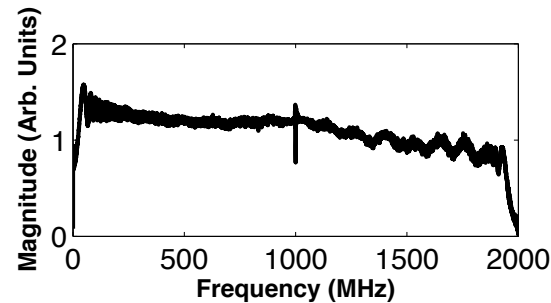
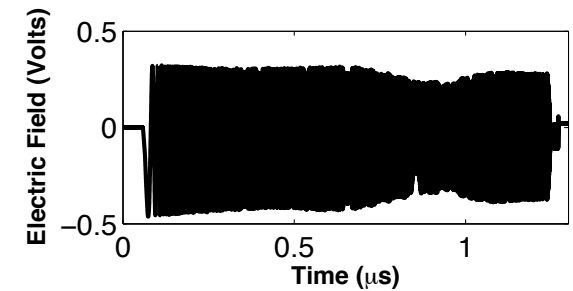
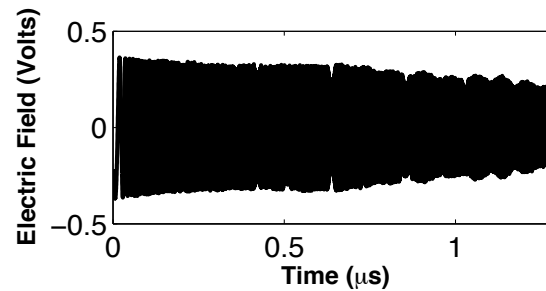
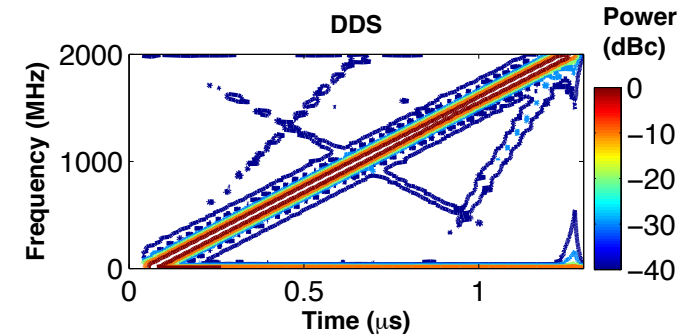
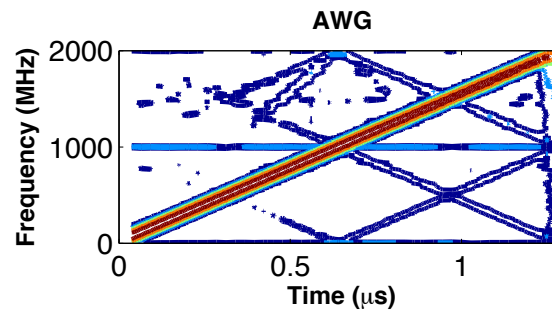
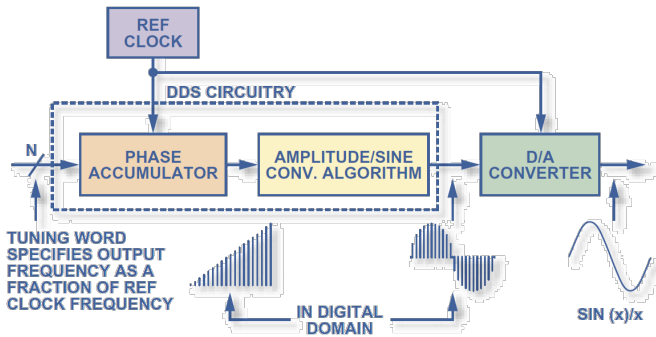
[C.Abeysekara, B. Joalland, N.M.Ariyasingha, L.N. Zack, I.R. Sims., R.W. Field, A.G. Suits, Journal of Physical Chemistry Letters, 2015]

# The Future of C-PUF

## Direct Digital Synthesis

Replacing AWG at low cost

Blake Group  
in Caltech



[I.A. Finneran, D. B. Holland, P. B. Carroll, and G.A. Blake, Review of Scientific Instruments, 2013]



# The Future of C-PUF

## *From GHz to THz: A Strong Overlap with Radioastronomy*

Observing facilities reach sensitivities to probe beyond simple molecules and on spatial resolution to reveal star and planet formation in action  
e.g. ALMA, NOEMA

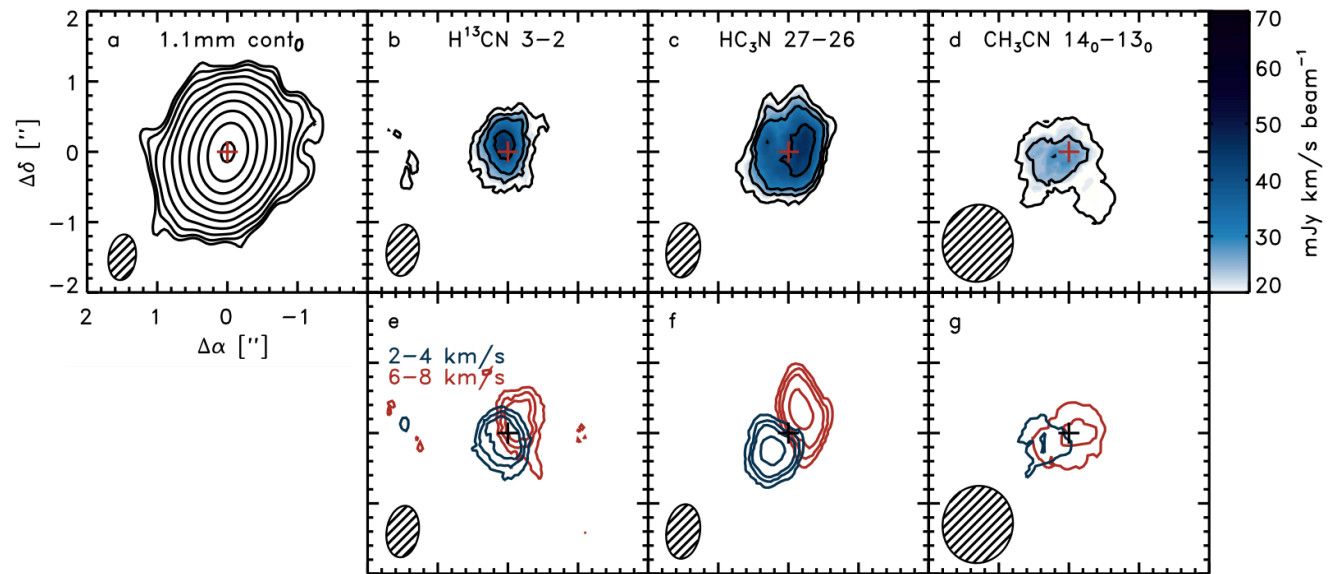
### ALMA:

85-950 GHz, up to ~10km baselines  
spatial resolution <0.1" at low frequencies

sensitivity to detect more complex low abundance species in star forming regions and disks

spatial distribution and kinematics of molecules within cores, embedded protostars and disks

=> pathways to molecular complexity



methyl cyanide in a protoplanetary disk

[Oeberg et al. 2015]

# Acknowledgments

## Prof. Arthur G. Suits



## Collaborators:

Prof. Robert W. Field (MIT)

Dr. G. Barratt Park (MIT)

Prof. Ian Sims (IPR/Rennes)

## Suits Group:

Chamara Abeysekera

Lindsay Zack

Nuwandi Ariyasingha

James Oldham

Kirill Prozument

WAYNE STATE  
UNIVERSITY



## Fundings:

