ERC Advanced Grant
CRESUCHIRP

Ultrasensitive Chirped-Pulse Fourier Transform mm-Wave Detection of Transient Species in Uniform Supersonic Flows for Reaction Kinetics Studies under Extreme Conditions

A short presentation of the project

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Summary

CRESUCHIRP

- CRESU technique for low temperature kinetics
- current challenges in chemical kinetics

CRESUCHIRP

- Chirped Pulse Fourier Transform Microwave (CPFTMW) technique
- a ground-breaking development in spectroscopy

CRESUCHIRP

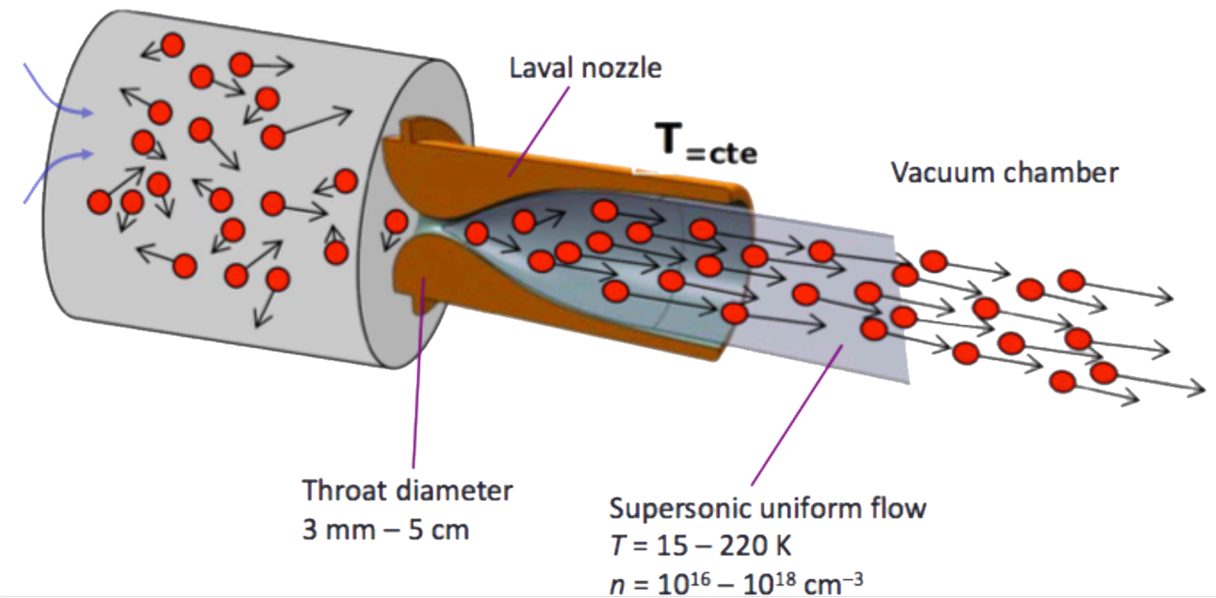
- Chirped Pulse in Uniform Flow (CPUF)
- a transformational technique for the study of chemical reactions

The ERC project

CRESUCHIRP

Cinétique de **R**éaction en **E**coulement **S**upersonique **U**niforme

- technique for cooling gases rapidly (few μs) down to as low as 5 K and studying reactions in the cold gas
- invented by researchers from the Department of Molecular Physics at the IPR (Descartes Prize, 2000 with the University of Birmingham)



Laval nozzle controls expansion of carrier gas: avoids problems of other cooling methods:

- expansion/cooling is rapid – condensation avoided
- expansion controlled – collisions maintain thermal equilibrium
- essentially a rapid temperature jump

- significant technical requirements (pumps, gases, technical support)
- enables measurement of very low temperature processes in the gas phase

The CRESU technique

Provides an ultra-low temperature thermalised (collisional) environment which can operate under heavily supersaturated conditions. It can be used for

Thermochemistry of weakly-bound systems e.g.

- **$OH + O_2 \rightleftharpoons HO_3$** (S. D. Le Picard, M. Tizniti, A. Canosa, I. R. Sims, and I. W. M. Smith, *The Thermodynamics of the Elusive HO_3 Radical.* **Science**, 328, 1258-1262 (2010).)

Cluster formation e.g.

- **water condensation** (J. Bourgalais, V. Roussel, M. Capron, A. Benidar, A. W. Jasper, S. J. Klippenstein, L. Biennier, and S. D. Le Picard, *Low Temperature Kinetics of the First Steps of Water Cluster Formation*, **Phys. Rev. Lett**. 116, 5, 113401 (2016).)

Low temperature reaction kinetics e.g.

- **understanding low temperature reactivity** (H. Sabbah, L. Biennier, I. R. Sims, Y. Georgievskii, S. J. Klippenstein, and I. W. M. Smith, Understanding reactivity at very low temperatures: The reactions of oxygen atoms with alkenes, **Science** 317, 102 (2007).
- **interstellar chemistry** (M. Tizniti, S. D. Le Picard, F. Lique, C. Berteloite, A. Canosa, M. H. Alexander, and I. R. Sims, Measurement of the rate of the $F + H_2$ reaction at very low temperatures **Nature Chemistry**, 6, 141-145 (2014).)

Challenges in gas phase chemical kinetics

Where are the **big challenges** in experimental gas-phase chemical kinetics now?

- **product channel specific** $k(T)$ over wide temperature ranges
- simultaneous coverage of species – **multiplex measurements**

In order to be sure to measure reliable elementary reaction rate constants for reactions, it is essential to **isolate the reaction**

- this requires **high sensitivity** in order to keep reactive (radical) concentrations low
- coupled with **good time-resolution**
- and the ability to measure either **absolute concentrations** or at the very least accurate **relative concentrations between different species**

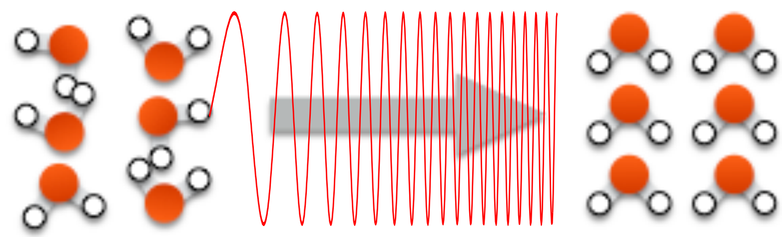
This places strong constraints on the detection techniques that are suitable for future experiments in gas kinetics

CRESUCHIRP

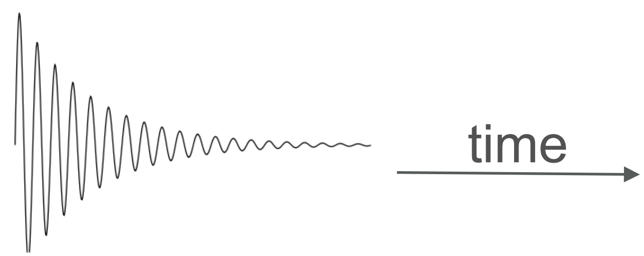
Chirped-**P**ulse **F**ourier-**T**ransform **M**icro**W**ave (CP-FTMW) Spectroscopy

- G. G. Brown, B. C. Dian, K. O. Douglass, S. M. Geyer, S. T. Shipman, and B. H. Pate, *A broadband Fourier transform microwave spectrometer based on chirped pulse excitation*, Rev. Sci. Instrum. 79, 053103 (2008).
- based on recent advances in high speed digital electronics for telecommunications (broadband arbitrary waveform generators and 'scopes)

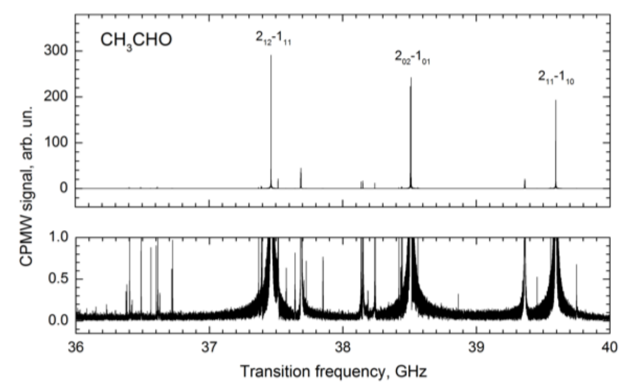
① Broadband excitation of any dipolar molecule with rotational transitions within frequency range of chirped pulse



② Detect the spontaneous emission (Free Induction Decay)



③ Fourier transform to obtain the spectrum



CP-FTMW Spectroscopy

Strengths

- **broadband advantage** – can detect any molecules with a dipole in range of (broad) frequency chirp – a **multiplex** technique
- **quantitative** – gives absolute concentrations of species present
- **specific** – rotational spectra are unique and non-overlapped
- **fast** – massive improvement in data collection speed compared to previous methods

CPFTMW is a transformational technique which has triggered a revolution in molecular spectroscopy

Weaknesses

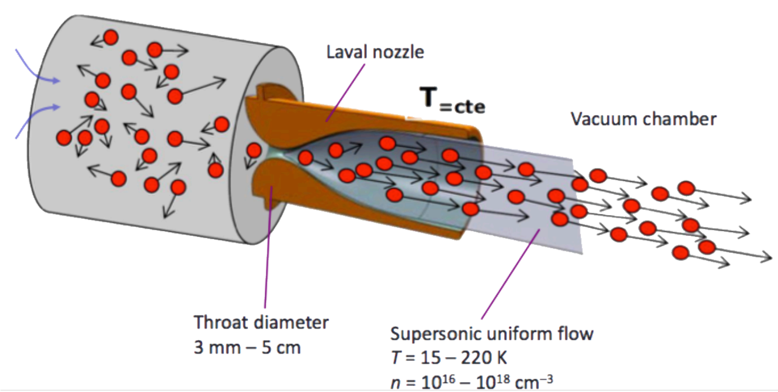
- relatively **low sensitivity** of rotational spectroscopy compared to other techniques such as LIF
- **high cost** of equipment (but the price is coming down)
- interpretation of rotational spectra requires **expert input**

CRESUCHIRP

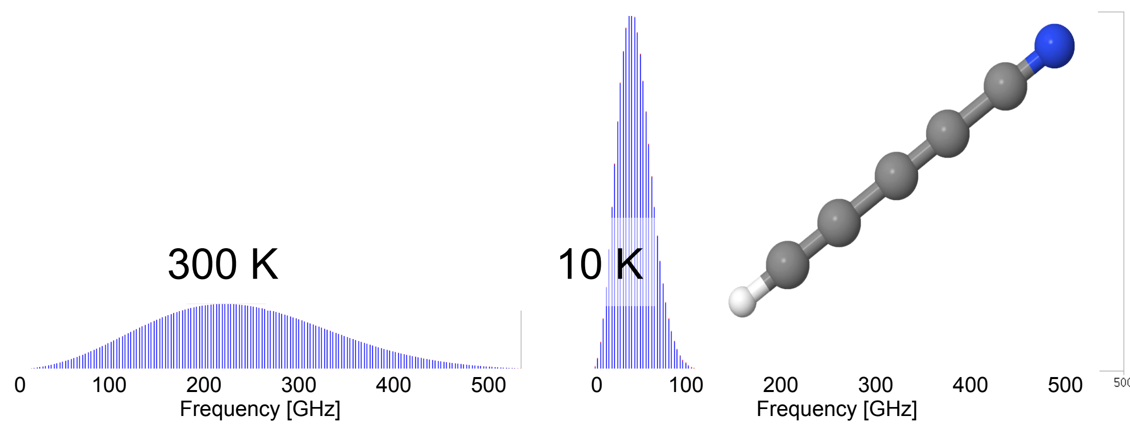
How do we maximize signal in chirped-pulse MW spectroscopy?

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

→ Population difference between adjacent rotational levels



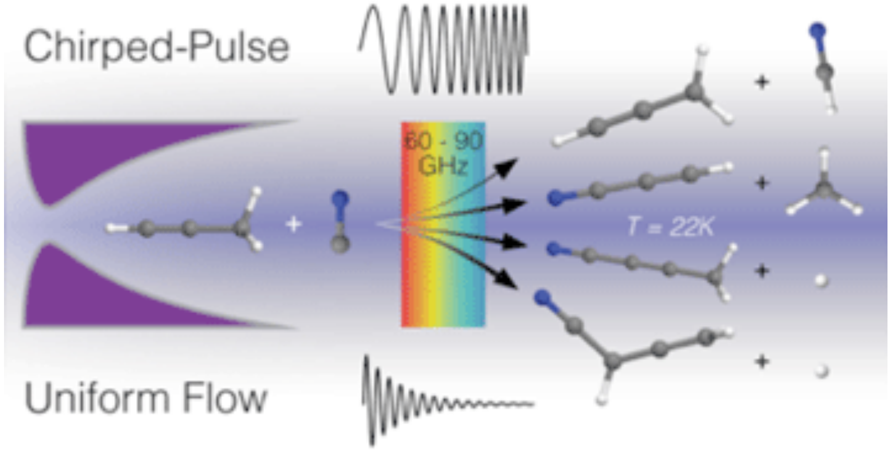
Uniform supersonic flow (CRESU) is an incredibly powerful **rotational refrigerator**



CRESUCHIRP

CPUF

Combine CRESU and CP-FTMW spectroscopy in new CPUF Chirped Pulse in Uniform supersonic Flow technique [1-3], developed in a collaboration led by Arthur Suits (U Missouri) with Bob Field (MIT) and Ian Sims (Rennes)



1. C. Abeysekera, et al., Product Branching in the Low Temperature Reaction of CN with Propyne by Chirped-Pulse Microwave Spectroscopy in a Uniform Supersonic Flow, J. Phys. Chem. Lett. 6, 1599 (2015).
2. J. M. Oldham, et al., A chirped-pulse Fourier-transform microwave/pulsed uniform flow spectrometer. I. The low-temperature flow system, J. Chem. Phys. 141, 7, 154202 (2014).
3. C. Abeysekera, et al., A chirped-pulse Fourier-transform microwave/pulsed uniform flow spectrometer. II. Performance and applications for reaction dynamics, J. Chem. Phys. 141, 214203 (2014).

CRESUCHIRP ERC project

Objectives:
"**to develop a revolutionary combination** of a chirped-pulse mm-wave rotational spectrometer with uniform supersonic flows generated by expansion of gases through Laval nozzles and **apply it to problems at the frontiers of reaction kinetics**, in particular **the determination of product channel-specific rate constants**, initially down to very **low temperatures**, for applications ranging from fundamental testing of chemical reaction rate theory through models of low temperature chemical environments such as dense interstellar clouds and extraterrestrial planetary atmospheres, through our own atmosphere and **eventually to higher temperature applications** in combustion and extrasolar planets."

In brief

- exploit superior continuous CRESU flows in Rennes to develop further the CPUF technique (**increase in sensitivity**)
- use the technique to address the major problem of **product branching ratios** in low temperature kinetics / astrochemistry
- combine it with a high enthalpy source to move to **high temperatures**

CRESUCHIRP ERC Team

The **project team**
the **PI Prof Ian Sims** (IPR), assisted by three senior colleagues,
Dr. Abdessamad Benidar (IPR)
Prof Robert Georges (IPR)
Dr. Sébastien Le Picard (IPR)
and (at least)
Two experienced 3-year postdocs and Three PhD students

External experts who have agreed to collaborate on the project include:
Dr L. Biennier (CNRS, IPR, Rennes)
Dr J-C Guillemin (CNRS, ENSCR)
Prof. L. Margules (Université de Lille 1)
Dr S.J. Klippenstein (Argonne National Laboratory, USA)