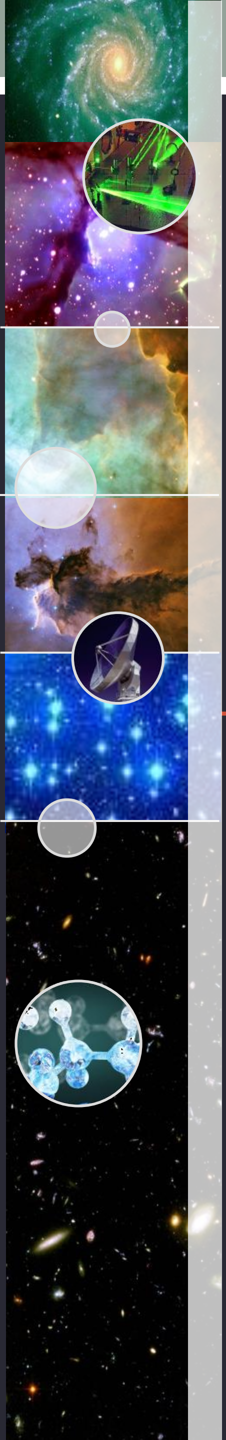
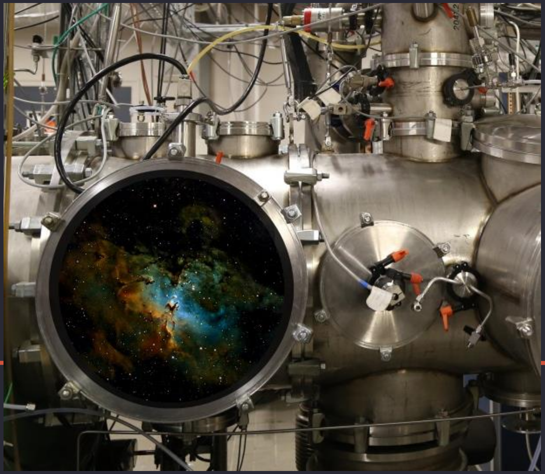


GAS PHASE CHEMICAL KINETICS : EXPERIMENTAL ADVANCES AND PROSPECTS



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Gas phase chemistry in the ISM

- The life cycle of molecules in the galaxy: a central question of modern astrophysics
    - Probing molecular complexity in star forming regions from the diffuse ISM to planetary systems

      → role of the molecules in star formation scenarios

      → history of the matter
    - Large diversity of molecules observed in the gas phase
        - Role of the gas phase chemistry
        - Role of the grains (formation, evaporation, condensation)
        - New observations, new questions: A. Bacmann et al. A&A 541, L12 (2012)
    - Chemical routes leading from atoms and diatomic molecules to complex organic species

Interstellar chemical modelling (1/2)

- Observations
  - Identification of molecules
    - Large fraction of molecules detected in cold cores of dense IS clouds
  - Estimation of abundances
    - Column density along a line of sight from rotational emission spectra
    - Conversion to a fractional abundance

Interstellar chemical modelling (2/2)

- Chemical modelling
  - Large networks of chemical reactions/physical processes (~ 4 500)
  - Experimental and theoretical support for obtaining information on these process at the temperatures prevailing in the ISM
    - Rate of these processes
    - Products of these processes
  - From a numerical point of view

$$\frac{dn_i}{dt} = \sum production - \sum destruction$$

Gas phase chemical processes in the ISM

- Ion-Neutral reactions ($A^{+,-} + B \rightarrow$ products)
- Neutral-Neutral reactions ($A + B \rightarrow$ products)
- Radiative association ($A^{(+)} + B \rightarrow AB^{(+)} + h\upsilon$)
- Dissociative recombination ($AB^{+} + e^{-} \rightarrow A^{+} + B$)

Gas phase chemical processes in the ISM

- Ion-Neutral reactions
- Neutral-Neutral reactions
- Radiative association
- Dissociative recombination

Rate coefficient

- Mainly bimolecular reactions in the ISM
- Rate of an elementary process = change of concentration with time

$$A + B \rightarrow C + D$$

$$-d[A]/dt = -d[B]/dt = +d[C]/dt = +d[D]/dt = k(T)\,[A]\,[B]$$

k(Temperature) : rate coefficient (cm^3 $molec^{-1}$ s^{-1})

Temperature dependence of the rate coefficient

- Difficult to predict, specially for neutral-neutral reactions

- The « shape » of the potential energy surface(s) describing the interactions between the colliders drives the temperature dependence of the rate coefficient

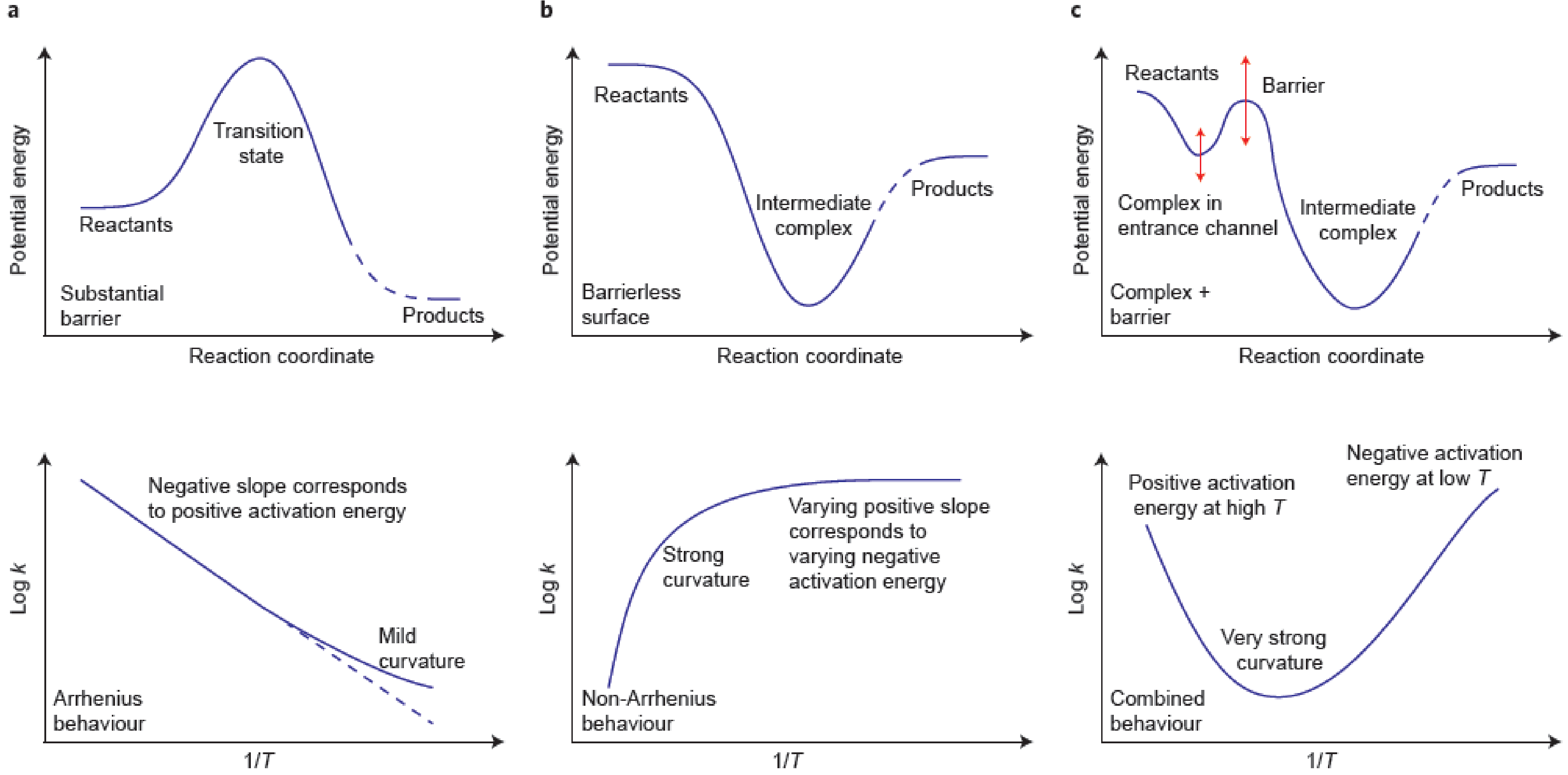


Figure 1 | General cases for exothermic reactions. To a good approximation, most chemical reactions adhere to the kinetics described by the Arrhenius equation, $k(T) = A\exp(-E_{act}/RT)$ where the temperature dependence of the rate constant is represented by a constant factor A multiplied by an exponential function. This function approximately represents the fraction of collisions at a given temperature T with enough energy to surmount the barrier, the magnitude of which is closely related to the activation energy E_{act}. A plot of the log of the rate constant as a function of inverse temperature should therefore be linear with a slope equal to $-E_{act}/R$, and is known as an Arrhenius plot. In this figure, the upper panels depict schematically the potential energy of the system as the reaction takes place, and the lower panels show how an Arrhenius plot might look for that system. **a**, A reaction with a substantial barrier, which adheres approximately to the Arrhenius equation. **b**, A reaction with no barrier, showing strongly non-Arrhenius behaviour. **c**, A reaction passing through an initial weakly bound complex and then over a barrier (which may or may not be above the reagent energy): the reaction adheres to the Arrhenius equation only at higher temperatures.

I.R. Sims, News&Views, Nature Chem. (5) 2013

Products of a reaction: branching ratio

- Some reactions form more than one set of products

$$A + B \rightarrow C + D \quad (a)$$

$$\rightarrow E + F \quad (b)$$

  - Overall rate coefficient $k = k_a + k_b$
  - Branching ratio of channel (a) : $k_a / (k_a + k_b)$

Determination of branching ratio and its temperature dependence presents one of the greatest challenges

Experimental reaction kinetics

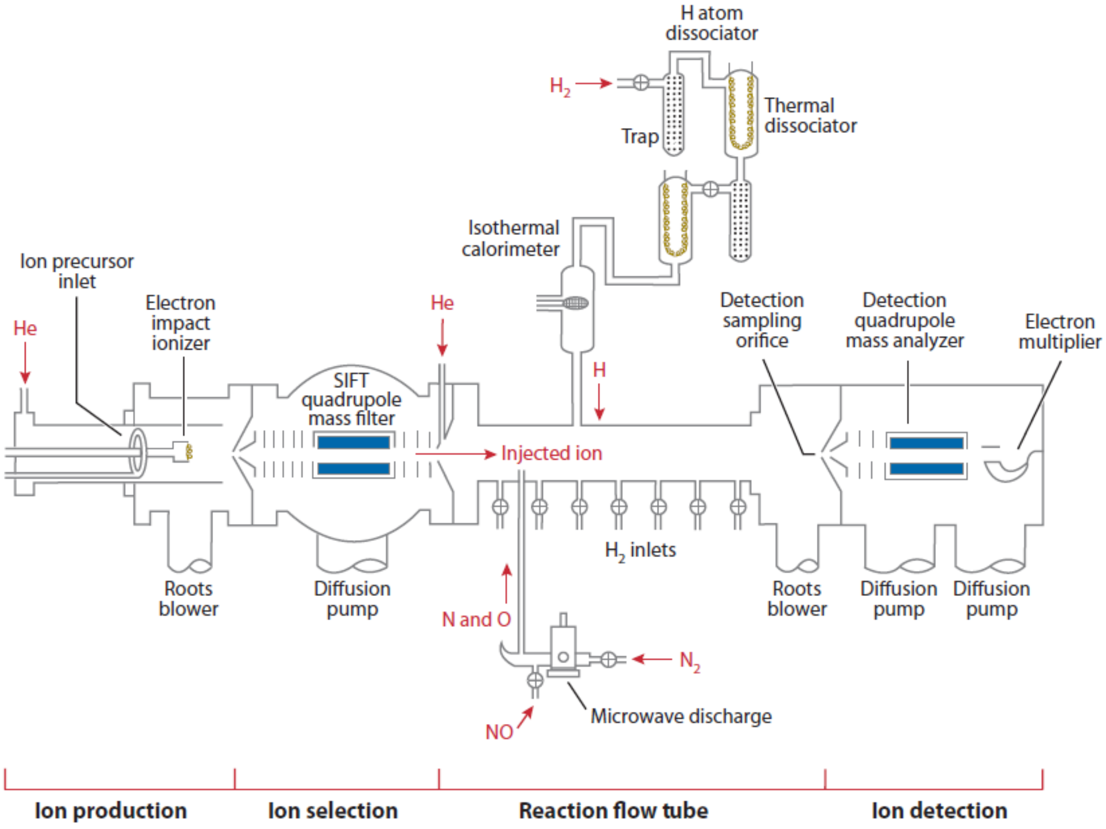
- Reactor (temperature)
- Production of species of interest
- Monitoring the concentration (relative or absolute) of one or more species during the reaction

Experimental reaction kinetics

- Ion-molecule reactions
  - (i)Trapping the ion in a field, adding excess of neutral, follow the loss of the ion (ii) Flow the ion down a gas-flow reactor
  - Most rate coefficients determined at room temperatures with the exception of cooled ion traps (Gerlich and co-workers) and CRESU experiments (Rowe and co-workers)
  - In principle, mass spectrometry can be used to determine rate and branching ratios.

Recent advances

The SIFT instrument at Boulder



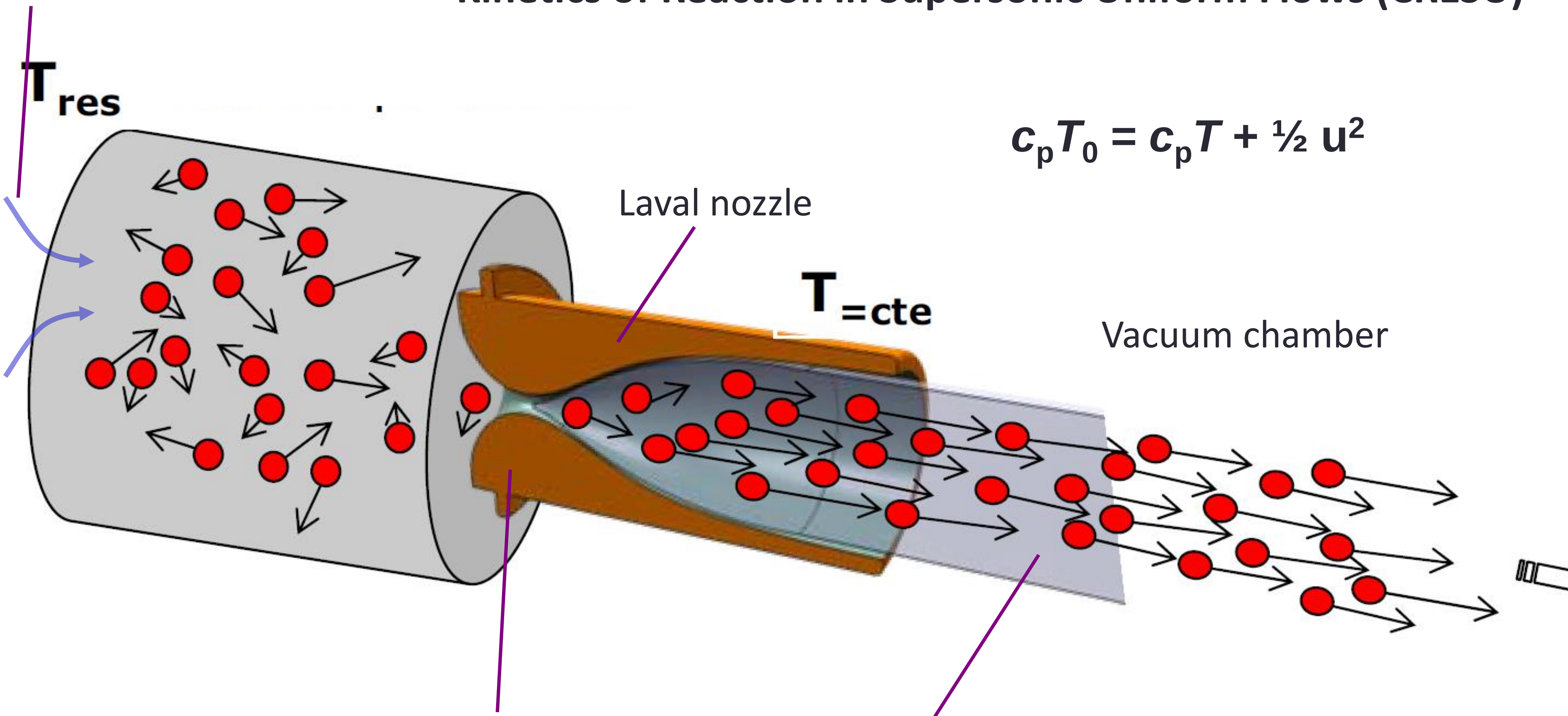
Snow an Bierbaum, Annu. Rev. Anal. Chem. 1:229-259 (2008)

Positive ions + H, N and O atoms – Negative ions + N and O atoms **at room temperature**

The CRESU technique at Rennes

Carrier gas (He, Ar or N_2) + reactants

Kinetics of Reaction in Supersonic Uniform Flows (CRESU)



$$c_pT_0 = c_pT + ½\,u^2$$

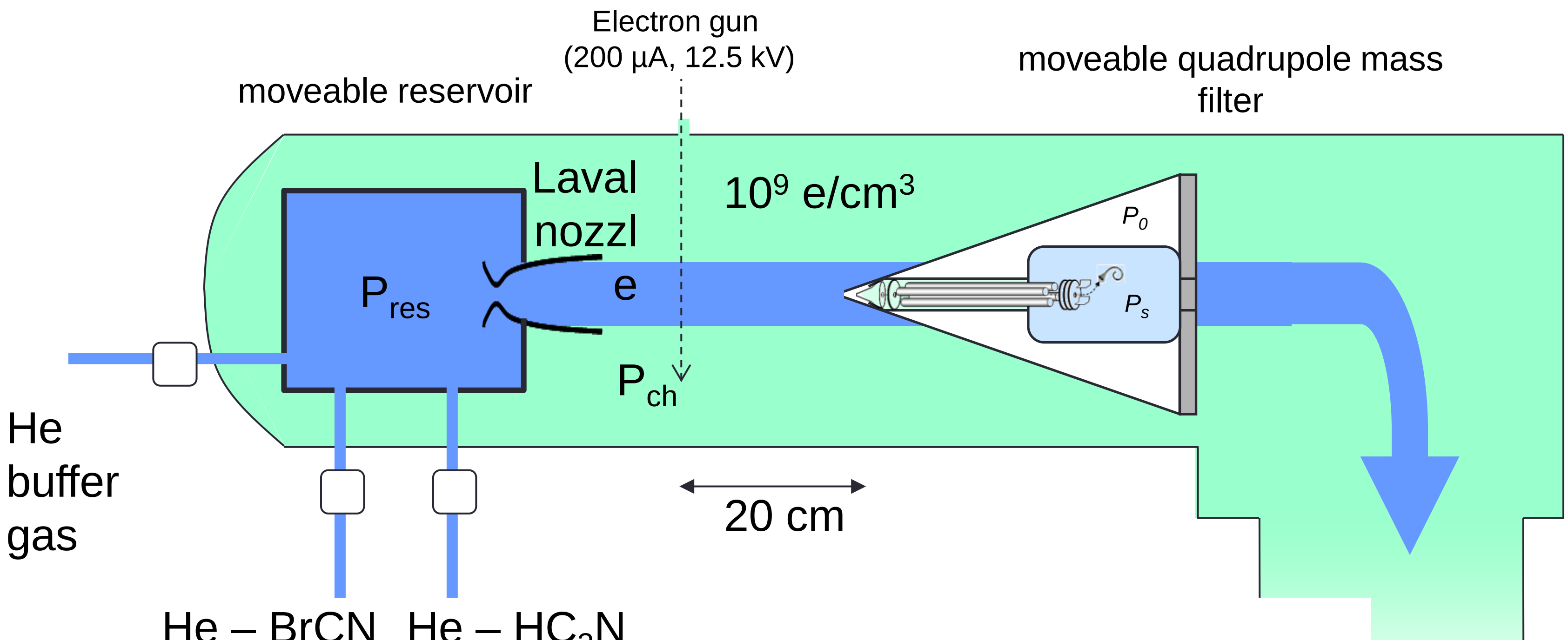
Laval nozzle

Vacuum chamber

Throat diameter
3 mm – 5 cm

Supersonic uniform flow
T = 15 – 220 K
n = 10^{16} – 10^{18} cm^{-3}

Kinetics of anion-molecule reactions at low temperature



Electron gun
(200 µA, 12.5 kV)

moveable reservoir

moveable quadrupole mass filter

Laval nozzl

10^9 e/cm^3

P_0

P_{res}

e

P_s

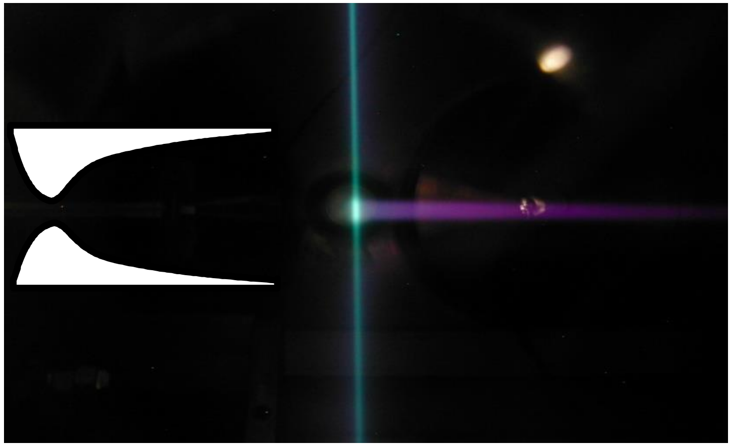
P_{ch}

He buffer gas

20 cm

He – BrCN mixture

He – HC_3N mixture



- CN^- + HC_3N (L. Biennier, S. Carles, J-C Guillemin et al. Icarus, 227, 123, 2014)
- C_3N^- + HC_3N (in progress)
- Collaboration with C. Alcaraz and co-workers (Orsay and Prague)

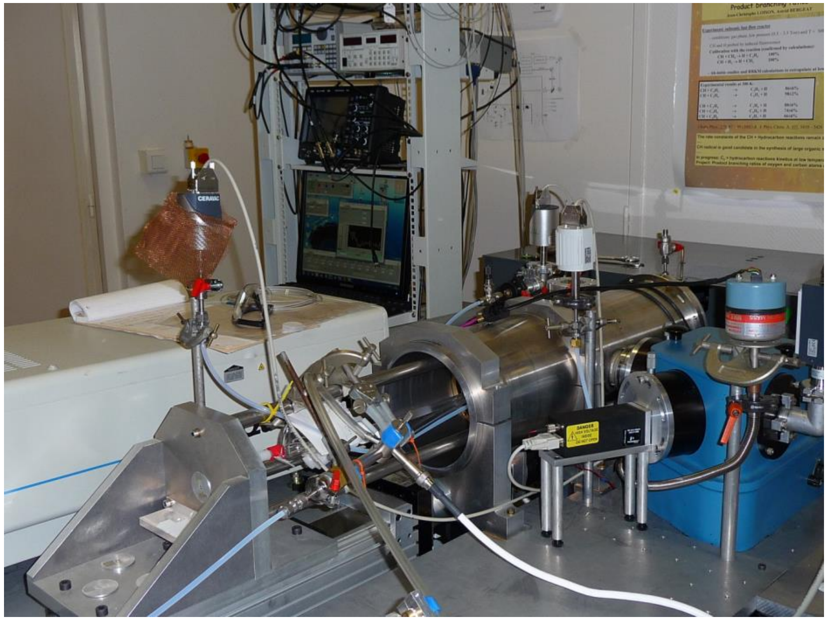
Experimental reaction kinetics

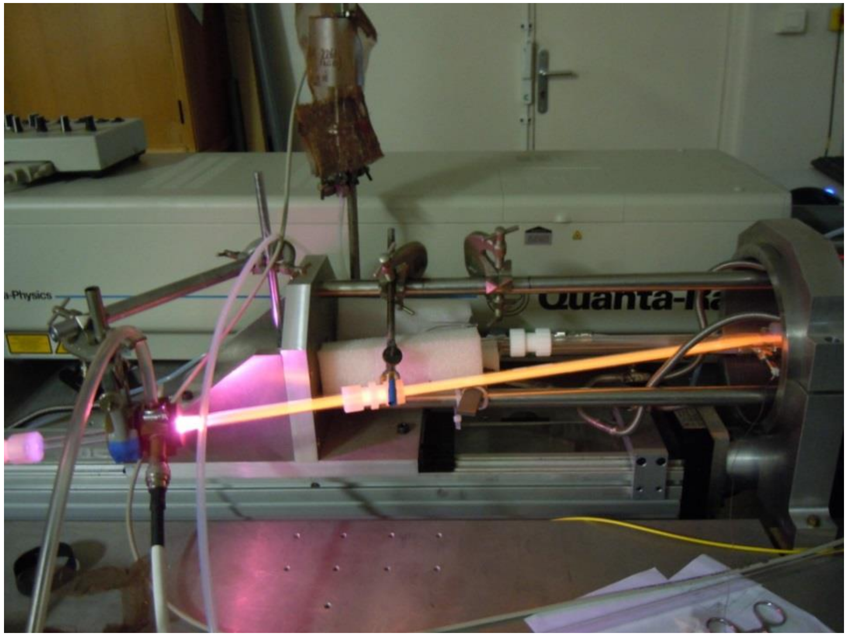
- Neutral-Neutral reactions
  - Flow the neutral species in a gas-flow reactor.
  - Cooled gas flow reactors and CRESU techniques
  - Flash photolysis/microwave discharge to generate radicals
  - Laser induced fluorescence (high sensitivity) or soft ionization/mass spectrometry techniques to monitor the loss of a reactant or the formation of products

Recent advances

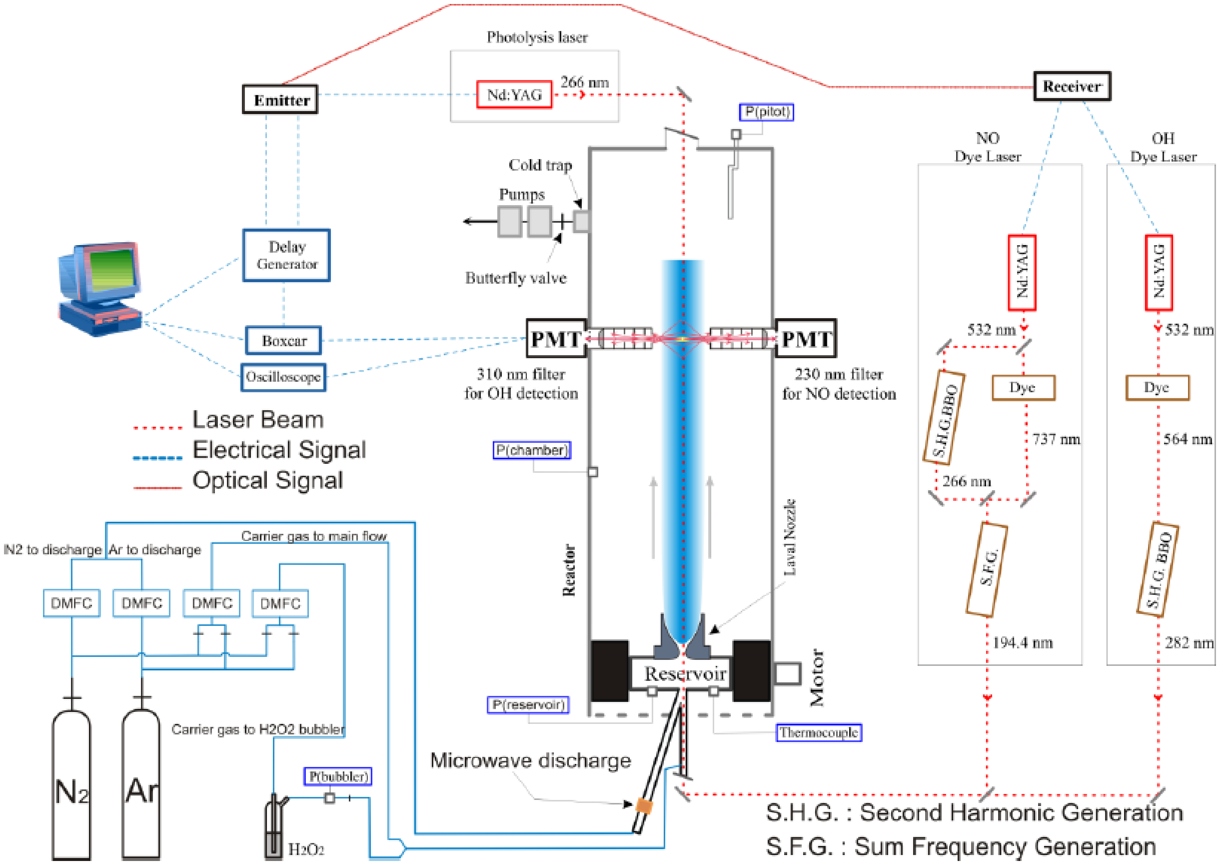
Radical-radical reactions at Bordeaux

- Coupling microwave discharge with CRESU technique





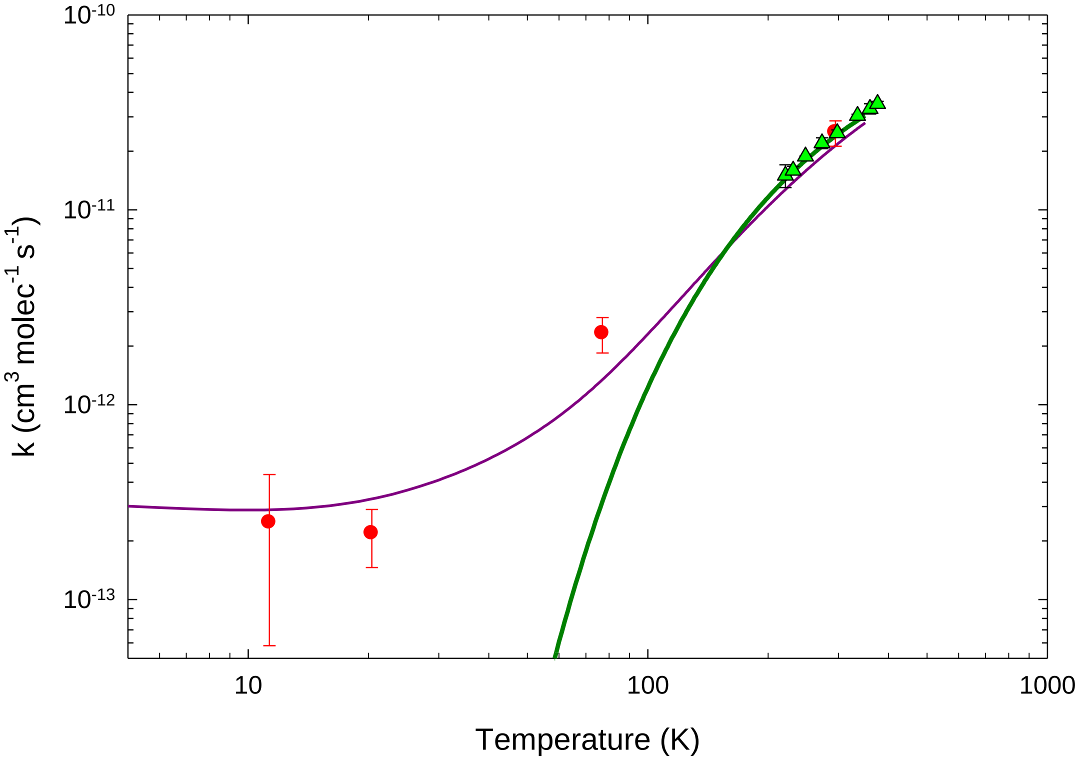
- Reaction of N + NO measured and used as a reference to measure N + OH kinetics (Daranlot et al. *Science 334, pp. 1538-1541, (2011)*).



(from J. Daranlot PhD thesis, 2012)

Tunneling in the F + $H_2 \rightarrow$ HF + H reaction at Rennes

- Hydrogen used as a buffer gas for supersonic expansion through Laval nozzles
- Tunneling effect observed



Tizniti et al. *Nature Chem.*, 6, 141 (2014)

Tunneling in OH + methanol reaction at Leeds

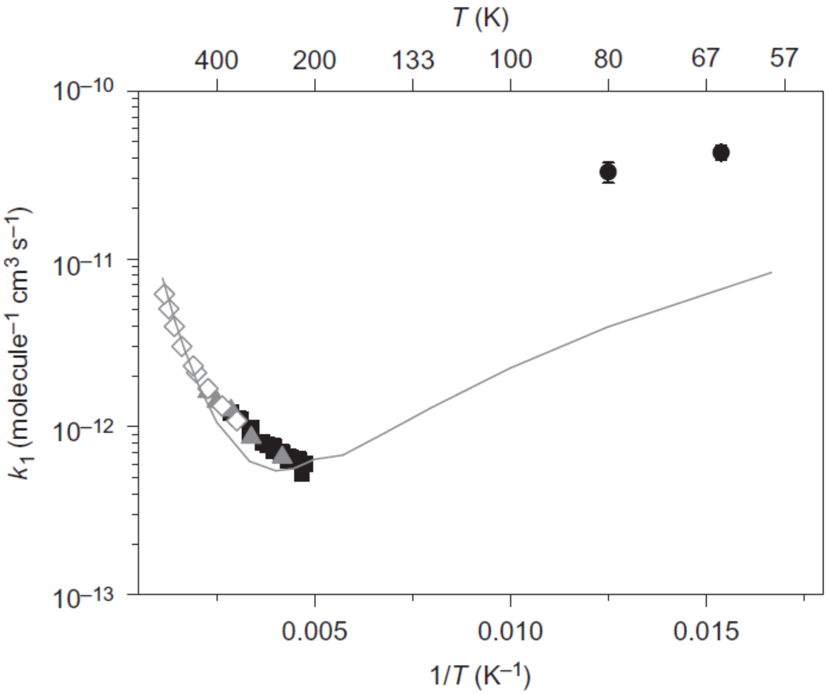
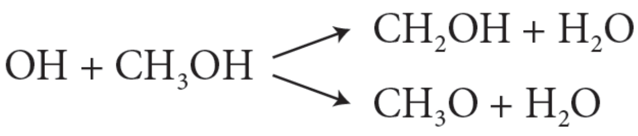


Figure 2 | Temperature dependence of the rate coefficient k_1 for the reaction of OH radicals with methanol, plotted in Arrhenius form together with a theoretical calculation. Data above 200 K are taken from a representative sample of literature data. Black filled squares, ref. 5; open diamonds, ref. 12; grey filled triangles, ref. 13. Black filled circles are experimental data from the current study, with 2σ error bars, and the data point at 82 K is an average of the three rate coefficients measured at different [N_2]. The solid line is the calculation using the master equation, incorporating QMT.

- Two possible channels



$$OH + CH_3OH \rightarrow CH_2OH + H_2O$$
$$OH + CH_3OH \rightarrow CH_3O + H_2O$$

- Both reactions have a substantial barrier

- Increase of the rate coefficient at very low temperature by two order of magnitude

Prospects

Ion-molecule reactions

- Chemistry of anions at room an low temperatures (Boulder, Rennes, Orsay)

- Branching ratios of ion-molecule reactions at low temperature (Rennes)

ANR CosChem (Rennes, Bordeaux, Le Havre, Madrid)

Neutral-Neutral reactions

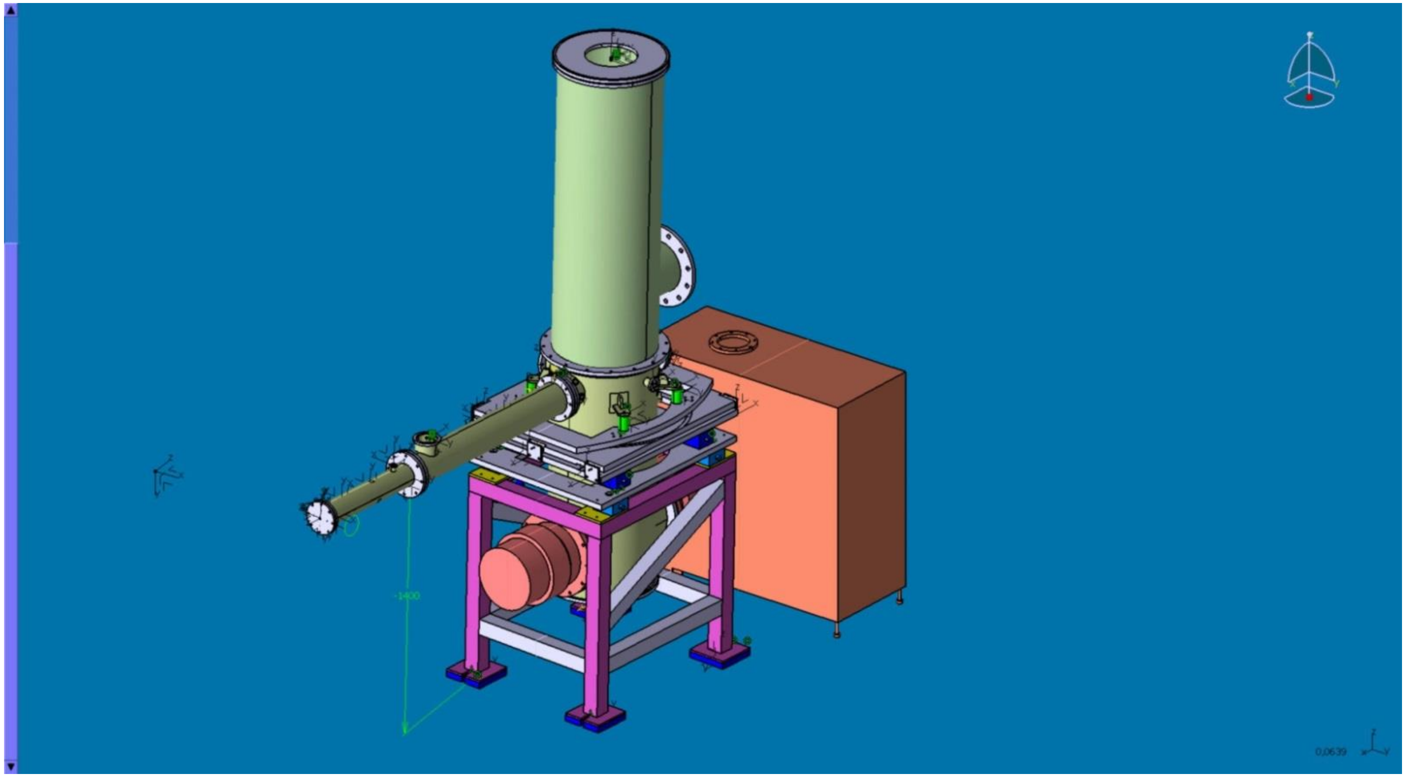
- Could tunneling effect operate more generally than expected ?

  → Explore the kinetics of chosen reactions and go to the lowest temperatures accessible by the experiments

- Branching ratio determination at low temperatures

ANR CRESUSOL (Rennes and SOLEIL)

- Kinetics and branching ratios determined using a pulsed CRESU apparatus coupled to synchrotron radiation (SOLEIL) and Time of Flight Mass Spectrometer



New techniques for new explorations (1/2)

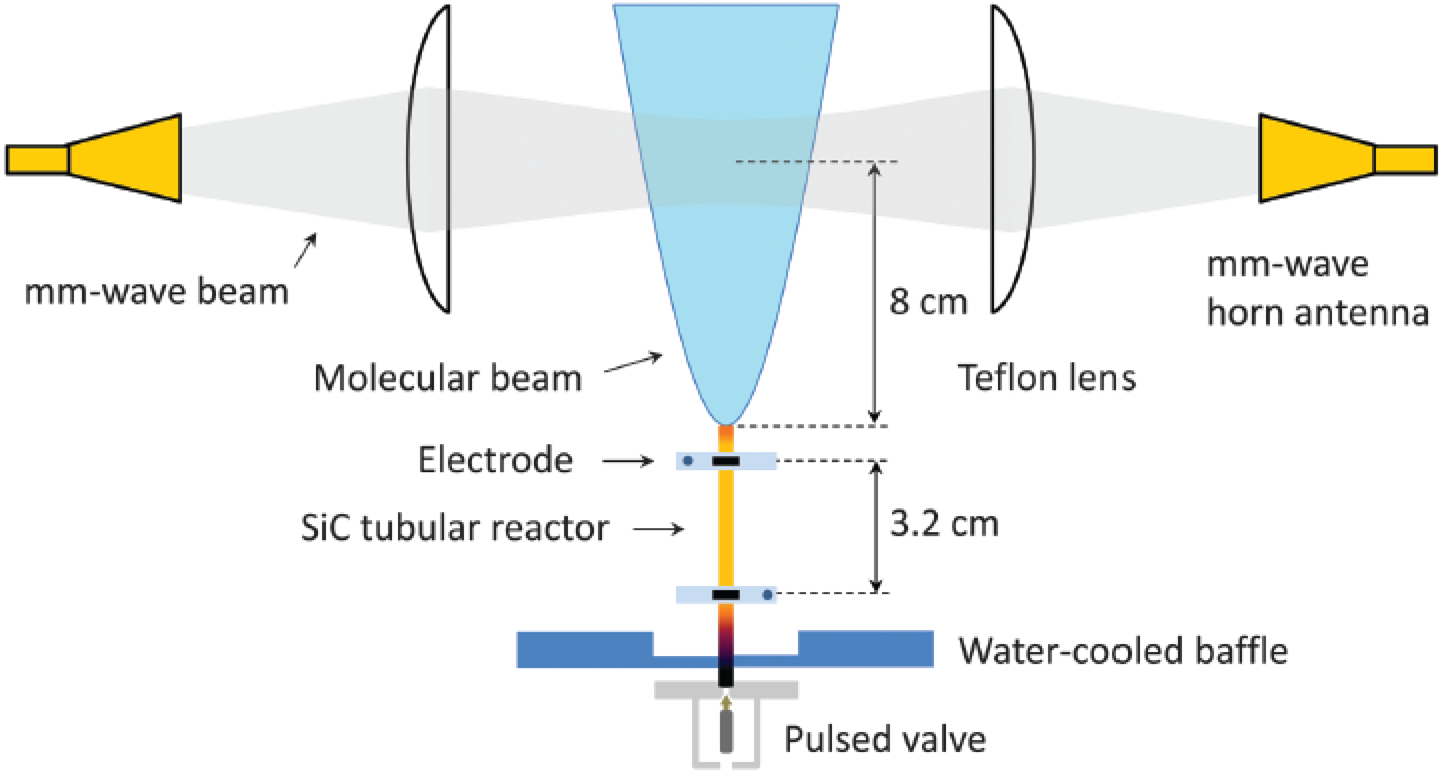
- The reactor : new pulsed versions of the CRESU techniques for reaction kinetics
    - Mark Smith, Steve Leone and Kevin Wilson at Berkeley (ALS)
    - Leeds group
    - Rennes group (PhD thesis S. Morales), exported to Ciudad Real (coll. A. Canosa)
    - A. Suits group at Wayne State University (coll. I.R. Sims)

New techniques for new explorations (2/2)

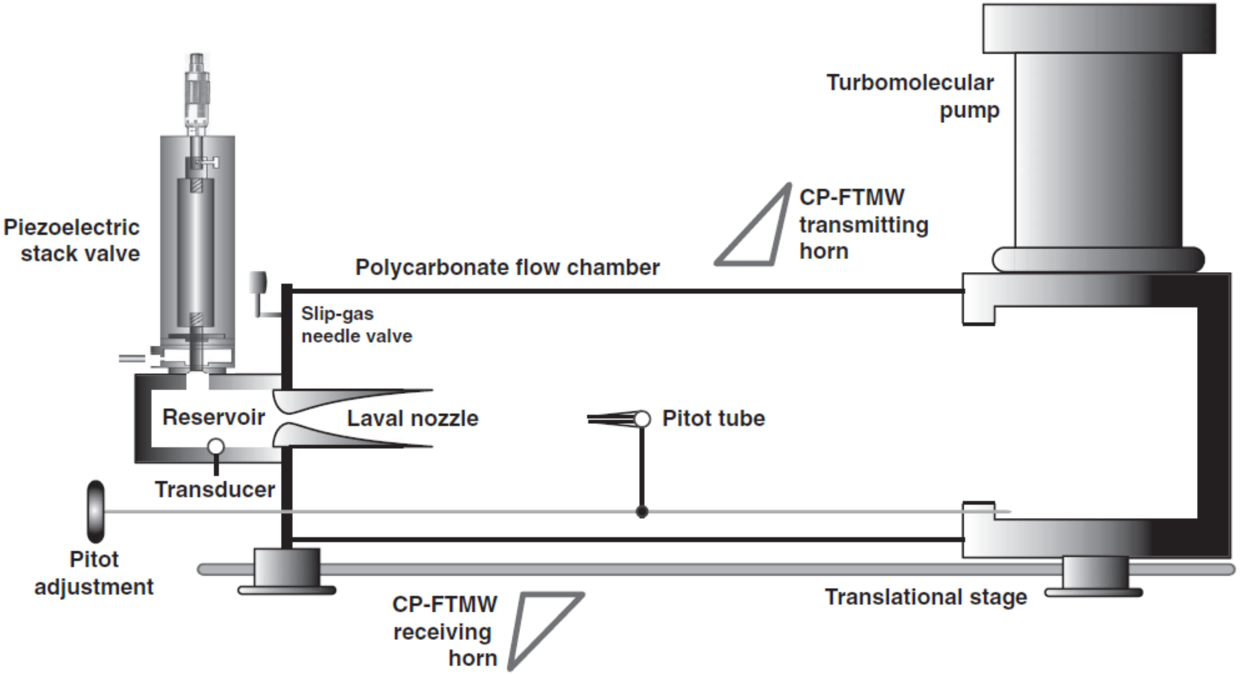
- New detection systems :
  - Soft ionization using synchrotron radiation coupled to mass spectrometry:

    → reaction kinetics and **branching ratios and isomer identification** using photoionization efficiency dependence on the photon energy
    - Taatjes et al. PCCP, **10**, 20 (2008),
    - Soorkia et al. Rev. Sci. Instrum. **82**, 124102 (2011)

  - Chirped-pulse millimeter wave spectroscopy
    - Spectral regions as broad as 10 GHz are covered in a single chirped pulse with high resolution (100 kHz) and meaningful relative transition intensities.
    - Due to its 1 part per million spectral resolution, pure rotational spectroscopy has exceptional precision for determining the structures of molecules and radicals.
    - unambiguous **assignment of molecules and radicals, distinguishing conformers and even enantiomers, vibrational states, and fine and hyperfine states**.



Prozument et al. PCCP 16, 15739 (2014)



Oldham et al. J.Chem. Phys. **141**, 154202 (2014)

A lot of new exciting results coming up!