

Focus on Laval nozzles kinetic experiments

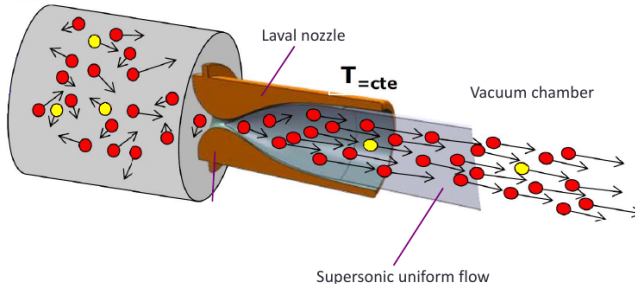
Olivier Durif

MPI FKF

January 21, 2026

How it all began ?

Why did someone decide at some point to perform a kinetic measurement in the gas phase in a supersonic Laval nozzle expansion ?



When and where it began ?

First publication : 1984.

Rowe, B. R. ; Dupeyrat, G. ; Marquette, J. B. ; Gaucherel.



Wind tunnel at The French Aerospace Lab (ONERA)

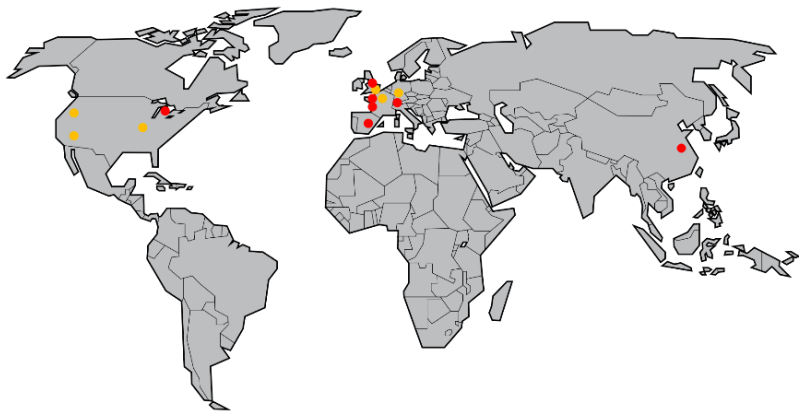
Nowdays : how everything continues (thanks to fundings)

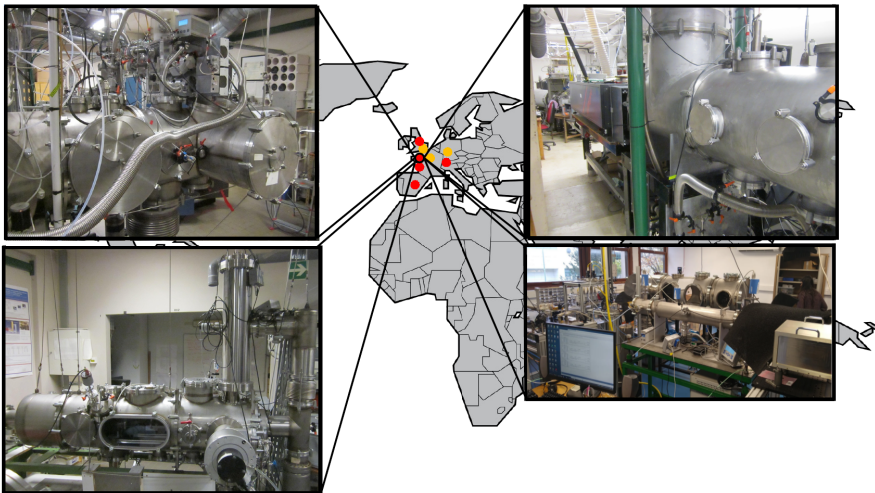
The reference reactor for gas phase studies at interstellar cloud temperatures

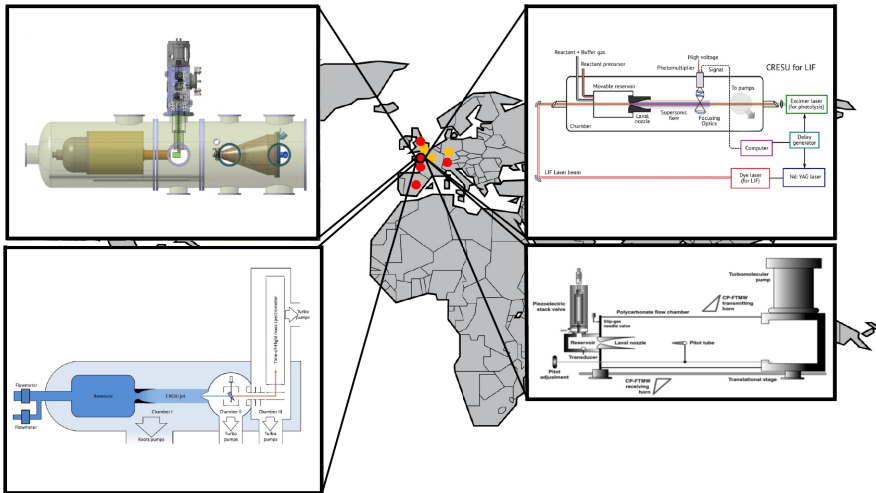
A versatile way to study gas phase chemical reactions at low temperatures

Key strengths :

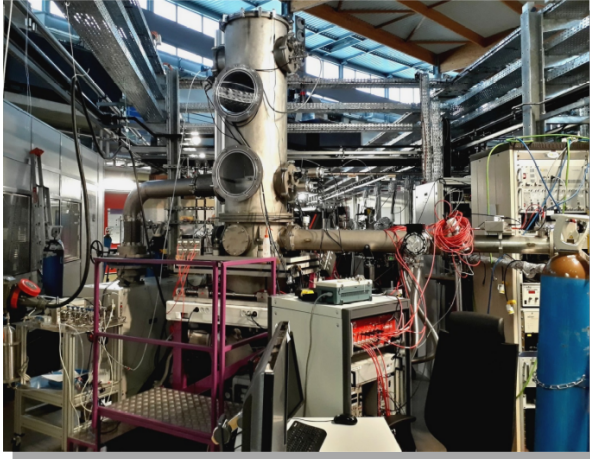
- ↪ Easy to build
- ↪ Wall less reactor
- ↪ Low temperature and thermal equilibrium
- ↪ High density
- ↪ Allow chemical kinetics
- ↪ Can be coupled to any detector/spectrometer







CRESU + SOLEIL = CRESUSOL

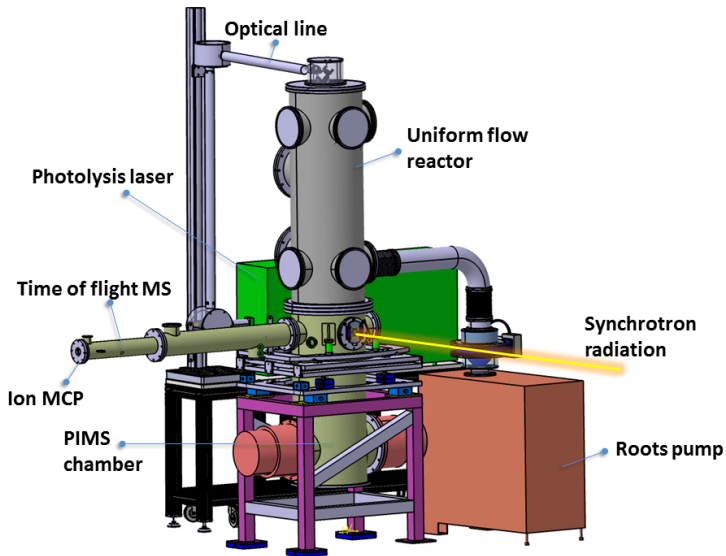


CRESUSOL on the DESIRS beamline (VUV) at SOLEIL

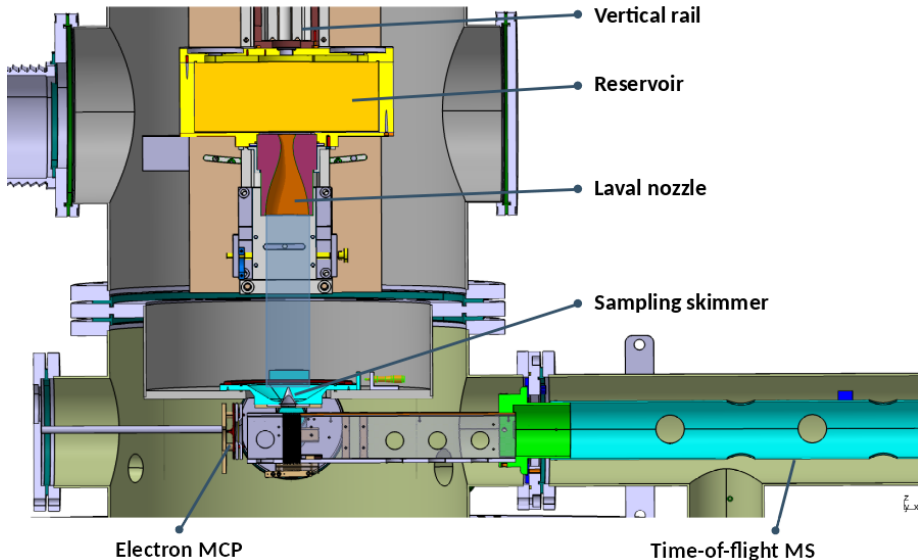


SOLEIL synchrotron

CRESUSOL setup

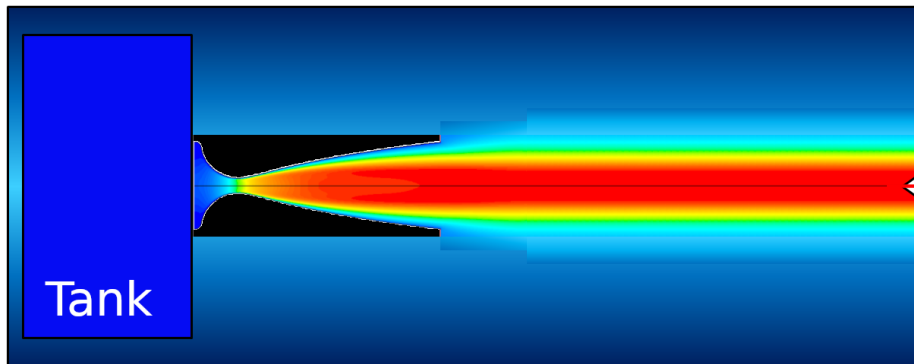


CRESUSOL setup



Uniform supersonic flow

Illustration of the Mach number of the flow



Total enthalpy conservation

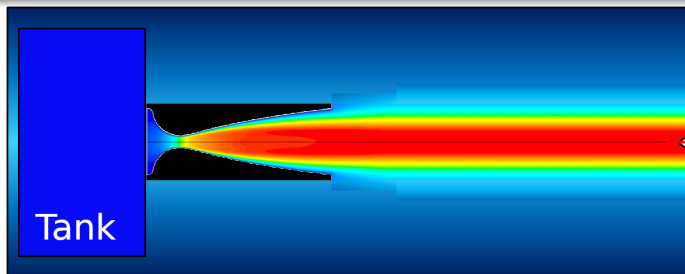
$$C_p T_0 = C_p T + \frac{1}{2} v^2$$

density 10^{16} cm^{-3}

temperature 10 – 100 K

uniformity $\sim 30 \text{ cm} \leftrightarrow \sim 500 \mu\text{s}$

How to make uniform supersonic flows ?



- direct calculation : Simulation by Navier-Stokes equations (CFD)
 - inverse calculation : Two-dimensional resolution of a profile by the method of characteristics
- Meudon historical approach : Owen's method with boundary layer correction by Michel's integral method (1960')

Program

<https://gitlab.com/odurif/cresu>

Design of de Laval nozzles for gas-phase molecular studies at very low temperature in uniform supersonic flow, O. Durif, Physics of Fluids, 2021

Parameters

Advanced Params

Carrier gas :

He

▼

Generating pressure (mbar) :

20

⬆️⬇️⬆️

Generating temperature (K) :

293

⬆️⬇️⬆️

Temperature (K) :

50

⬆️⬇️⬆️

Mach :

3,8183766184

⬆️⬇️⬆️

Pressure (mbar) :

0,2405946443

⬆️⬇️⬆️

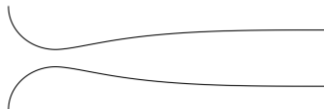
Density (1e-16 cm-3) :

3,4843540088

⬆️⬇️⬆️

✓ Validate

Result :

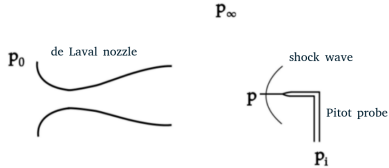
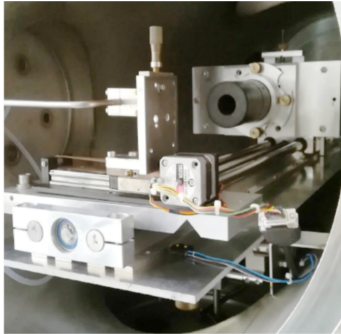


Solving method :

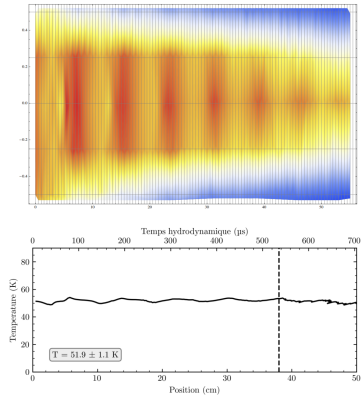
- perturbation analysis
- method of characteristics

Pitot characterization

Pitot system



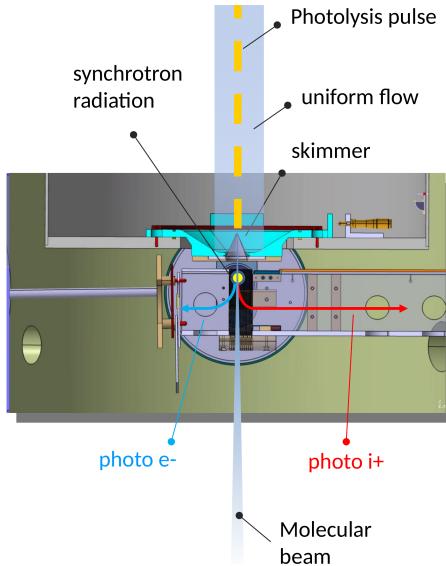
flow mapping



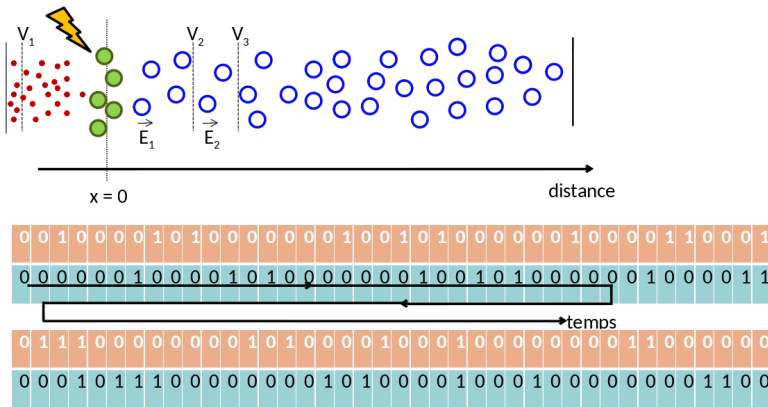
Rayleigh formula

$$\frac{P_i}{P_0} = \left(\frac{(\gamma+1)M^2}{(\gamma-1)M^2+2} \right)^{\frac{\gamma}{\gamma-1}} \left(\frac{\gamma+1}{2\gamma M^2 - (\gamma-1)} \right)^{\frac{1}{\gamma-1}}$$

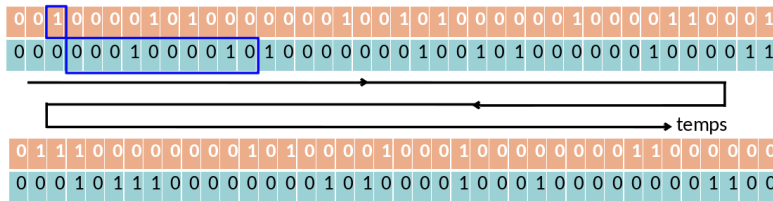
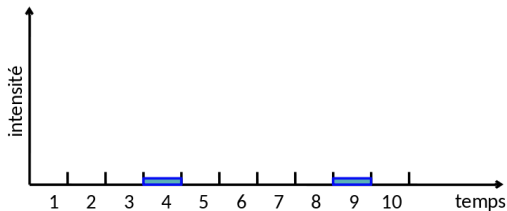
CREUSOL spectrometer



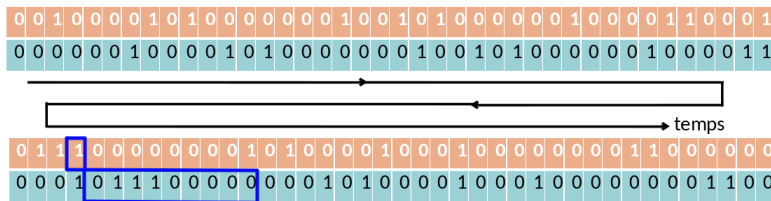
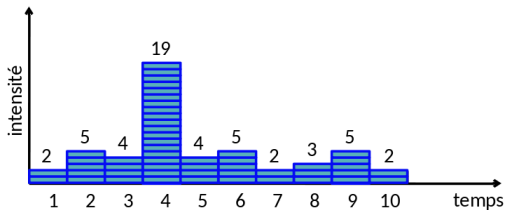
Acquisition principle



Acquisition principle



Acquisition principle

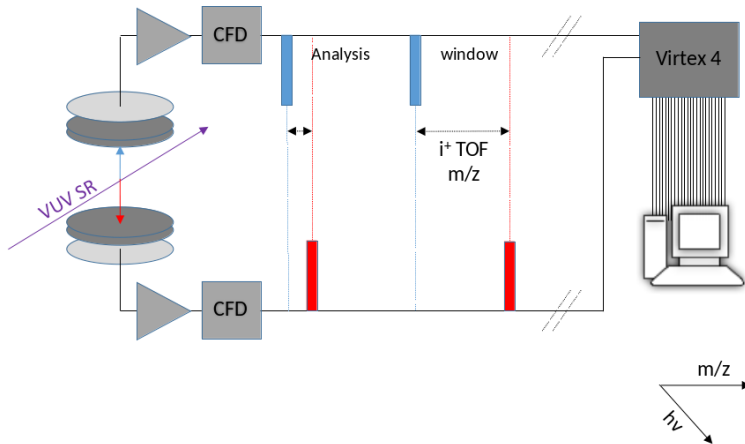


Acquisition scheme

Two possible configurations for the time measurement :

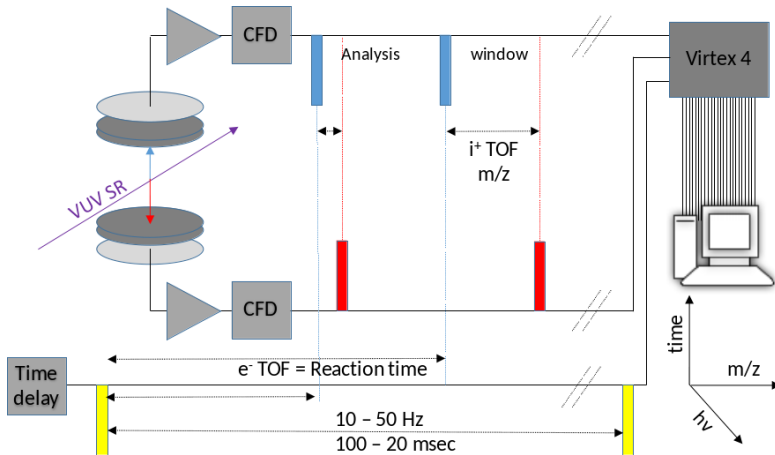
- ① Molecular clusters : continuous ion/electron acquisition with kinetic time resolution by nozzle displacement
- ② Chemical reactions : internal counting triggered by the excimer laser

Acquisition scheme



Multistart-multistop acquisition

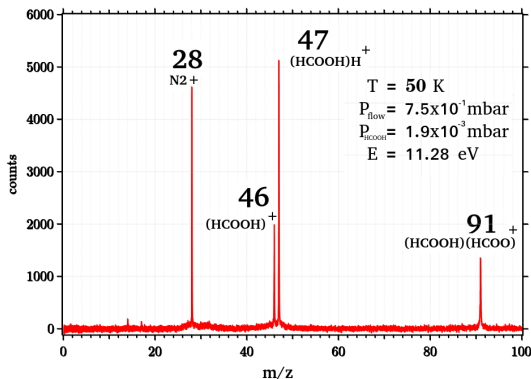
Acquisition scheme



Multistart-multistop scheme (O. Durif, & al., RSI, 2021)
with electron time stamping

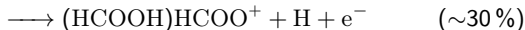
Photoionization of formic acid

Mass spectra of the monomer and the dimer

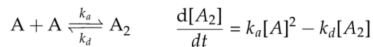
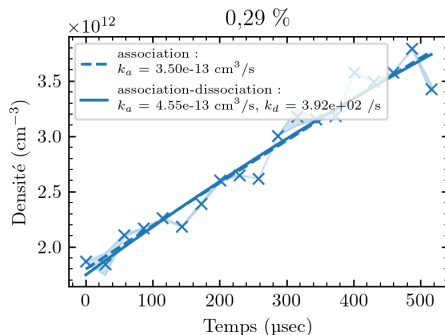
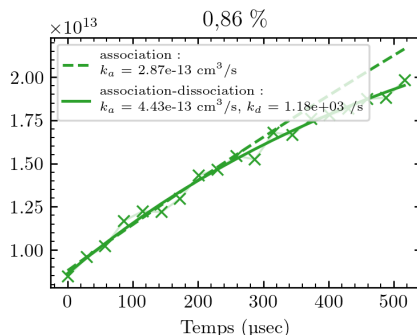


Photoionization of the monomer : $HCOOH + h\nu_{11.28 \text{ eV}} \longrightarrow (HCOOH)^+ + e^-$

Photoionization of the dimer :

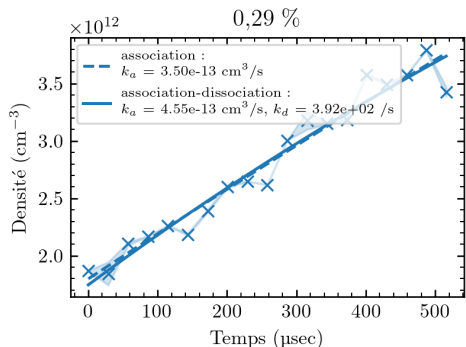
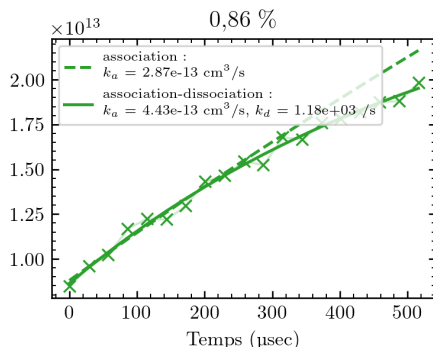


A kinetic trace



How should this be interpreted? Has a balance between association and dissociation been reached? Really?

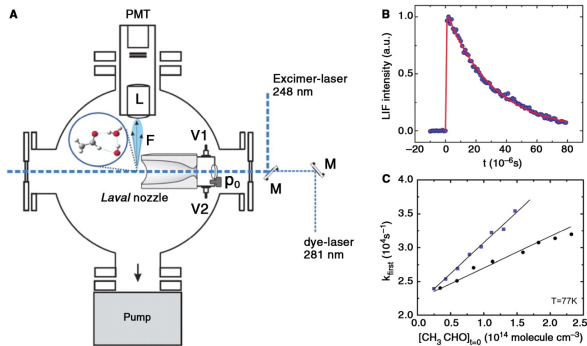
A controversial topic



An alternative interpretation of these kinetic traces : the density drops at a long distance from the nozzle outlet and the measurement is taken outside of uniform conditions.

It took me months to admit this after my PhD, and my former colleagues still haven't admitted the reality of the data....

A fresh look at old data

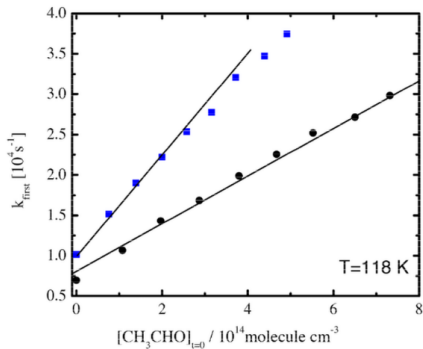
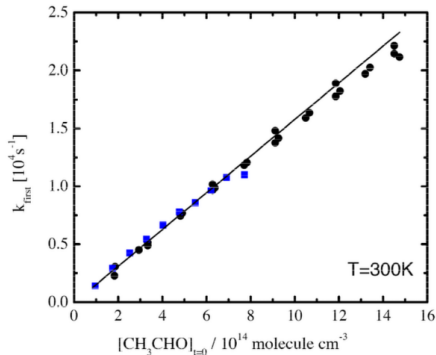


Water Catalysis of a Radical-Molecule Gas-Phase Reaction, Vöhringer-Martinez et al, Science, 2007

Authors' highlight

"The results suggest that even single water molecules can act as catalysts in radical-molecule reactions."

A typical result



SI : Water Catalysis of a Radical-Molecule Gas-Phase Reaction,
Vohringer-Martinez et al, Science, 2007

The Subject of the Controversy

Uniform flow means diffusion is negligible.

J. Chem. Soc., Faraday Trans. 2, **1989**, **85**(10), 1631–1641

Mass-selected Ion-Molecule Reactions at Very Low Temperatures

The CRESUS Apparatus

Bertrand R. Rowe, Jean-Baptiste Marquette and Christiane Rebrion

Laboratoire d'Aérothermique du CNRS, 4ter route des Gardes,
92195 Meudon Cedex, France

However, another characteristic of uniform supersonic flows has to be considered, i.e. that the diffusion is negligible. Thus, owing to collisions, a gas particle injected through

It's all become a great nonsense.

Kinetic Study of the Reactions of Ground State Atomic Carbon and Oxygen with Nitrogen Dioxide over the 50–296 K Temperature Range

Kevin M. Hickson* and Jean-Christophe Loison

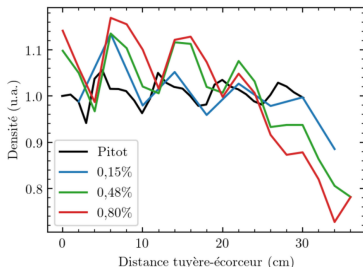
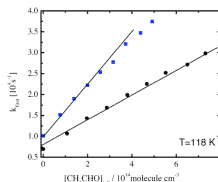
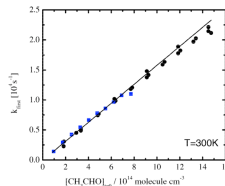
 Cite This: *J. Phys. Chem. A* 2024, 128, 10598–10608

 Read Online

It can be seen from [Figure 1](#) that when NO₂ is absent from the reactor, as shown by the red data points in [Figure 1](#), the C fluorescence signal decays at a nonnegligible rate. In this case, C atoms are lost through several secondary processes such as diffusion out of the observation zone (but still within the supersonic flow) with a first-order rate constant k_{diff} and

The point of contention

Results are driven by diffusion, not by chemical reactions !
reagent concentration increase $\propto$ Temperature increase $\Rightarrow$ flow density drop.



Problem illustration. Data from
Vöhringer-Martinez (Science, 2007).

Durif's Ph.D. Manuscript, 2019.

$\Rightarrow$ New interpretation of $> 99\%$ of chemical kinetics results in this research field.

More data with a different perspective

.5 Clustering experiment in the Ar 30 K nozzle

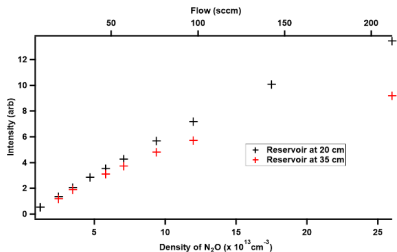


Figure 18: Clustering test in the Ar 30 K nozzle using N_2O $J = 3-0$ transition.

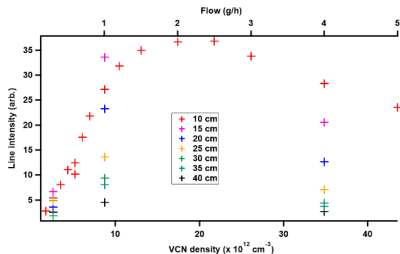


Figure 19: Clustering test in the Ar 30 K nozzle using acrylonitrile $J_{Ka,Kc} = 80,8-70,8$ transition

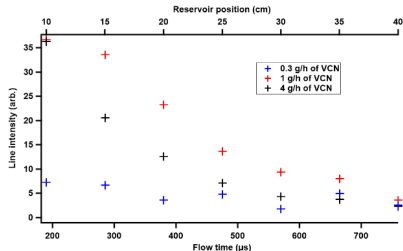


Figure 20: Clustering test in the Ar 30 K nozzle using acrylonitrile $J_{Ka,Kc} = 80,8-70,8$ transition changing the position of the reservoir at constant flow of acrylonitrile

Data in a Laval nozzle expansion by
Chirped-Pulse Spectroscopy

Appendix at T. Guillaume, 2021

- The reaction kinetics at low temperatures (<100 K) are probably not as interesting as was believed based on measurements taken over the past 30 years.
- From the kinetic rates constants reported so far in about 200 studies published in the literature, I predict that we will never observe the expected products in the expected proportions.
- The behavior of these “uniform” expansions involving gaseous mixtures is a complex topic.
- Changing science takes time.
- Let's not be mistaken : the idea of using dense, cold expansions to thermalize molecules is incredibly rich and exciting.