# A Critical Reappraisal of Low-Temperature Kinetics in Uniform Supersonic Flows

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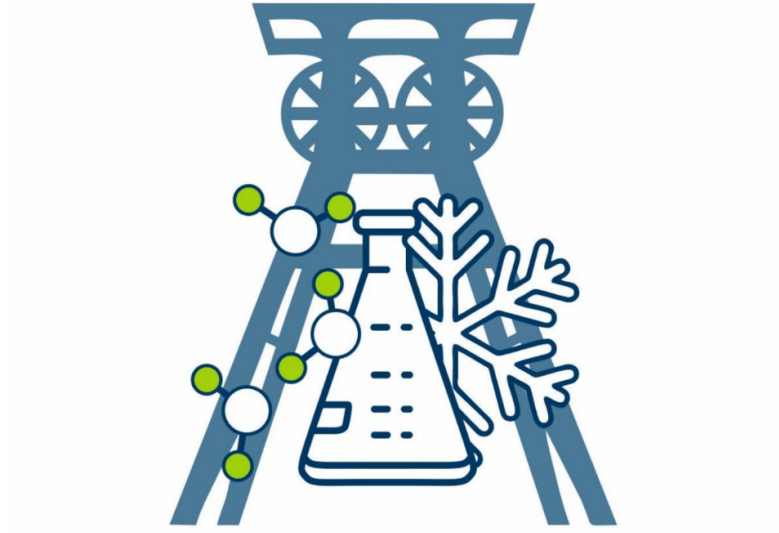
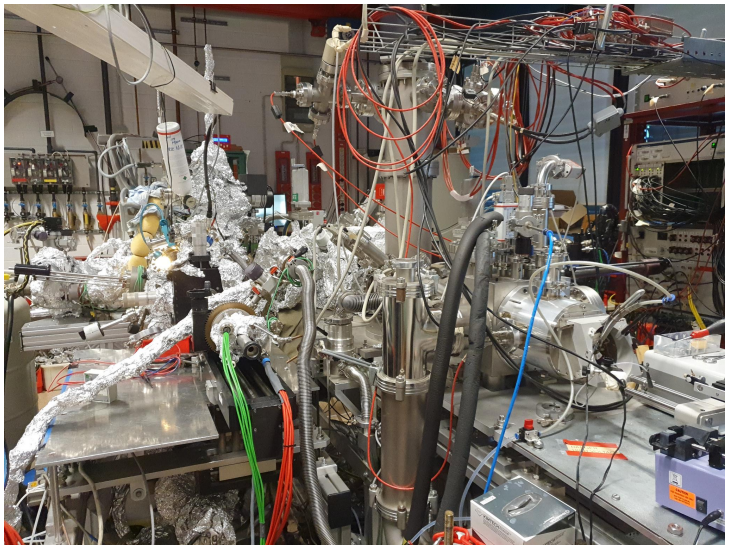


# Acknowledgments



ESIBD+STM setup at MPI-FKF

Dr. Kelvin Anggara
Group Leader at MPI FKF and
Prof. at Hong Kong University


Kumar, *Nat. Rev. Phys.* (2026)

Wu *et al.*, *ACS In Focus* (2025)

# A question to the scientific community

**Can astronomical observations be used to constrain crucial chemical reactions? The methoxy case. SOLIS XVIII**

Nadia Balucani ✉, Cecilia Ceccarelli ✉, Fanny Vazart, Francois Dulieu, Dimitrios Skouteris, Marzio Rosi, Fernando Pirani, Eleonora Bianchi, Paola Caselli, Claudio Codella

*Monthly Notices of the Royal Astronomical Society*, Volume 528, Issue 4, March 2024, Pages 6706–6719,

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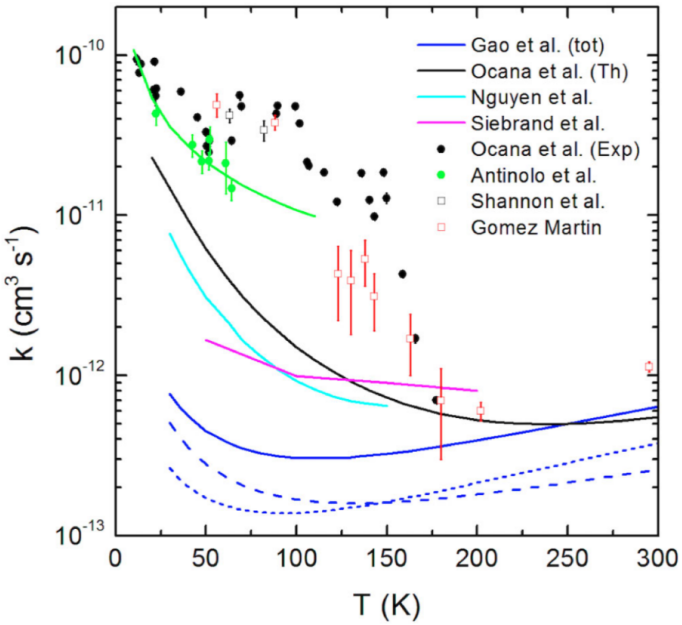


# The verdict, in numbers

$$CH_3OH + OH \xrightarrow{k} CH_3O + H_2O$$

| **Rate coefficients** | $T \approx$ **50–100 K** (protostellar envelopes) |
|---|---|
| Experimental — AAJ2016 (CRESU) | $\times$10 too high |
| Theoretical — Gao et al. (2018) | ✓ agrees |

> *"The model predictions obtained using the theoretical rate coefficients by Gao et al. (2018) are in agreement with the observations, whereas those obtained using the value by AAJ2016 fail to reproduce the observations by about a factor of 10."*
>
> *"The comparison between the astrochemical model predictions and observations seems to favour the theoretical calculations by Gao et al. (2018)."*

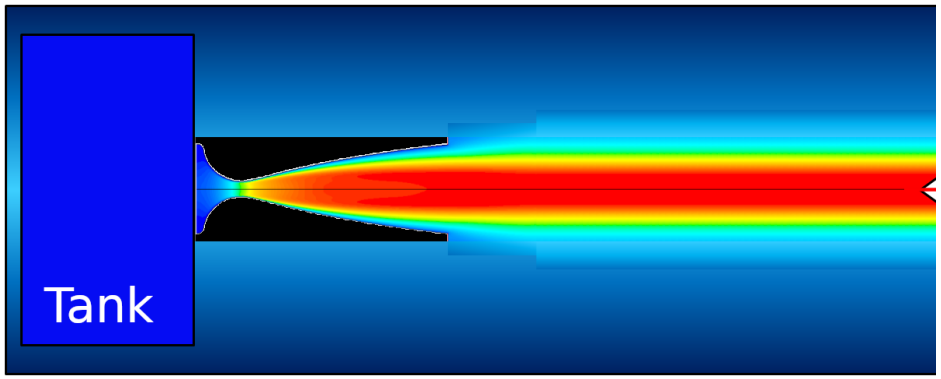
— Balucani et al., MNRAS 528, 6706 (2024)

# The bottom line

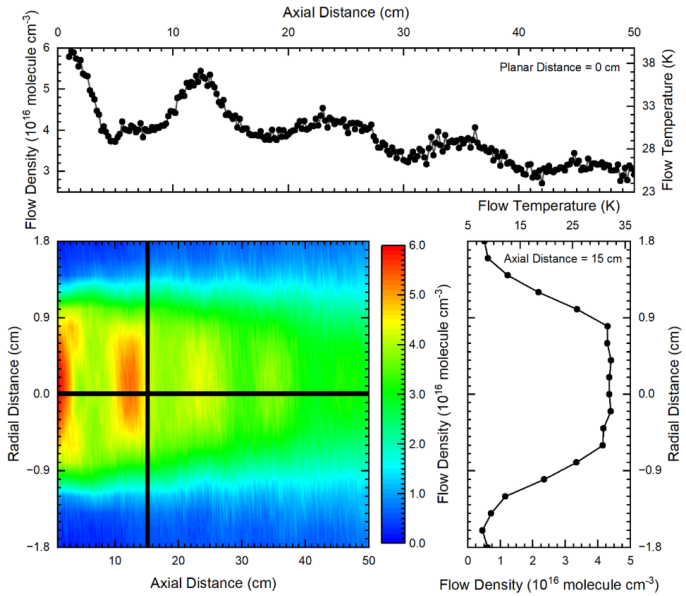
- We are facing a major problem in the field of low-temperature chemical kinetics
- Laboratory rate coefficients are largely **overestimated**
- Cause : the density drop of the flow induced by gas mixing

$\Rightarrow$ In my view, this field needs to be **rethought**

# The CRESU principle in one picture



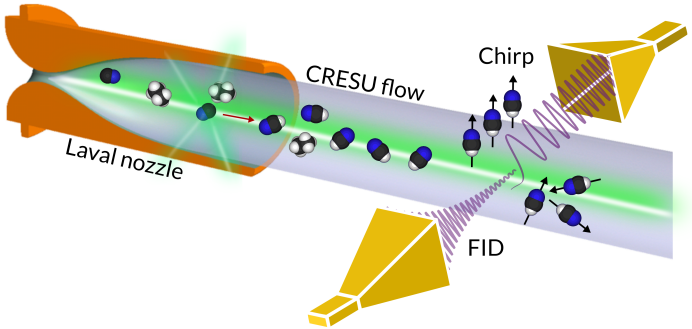

Energy conservation : $C_p T_0 = C_p T + \frac{1}{2} v^2$




Lucas et al., J. Chem. Phys. (2024).

The whole method relies on a simple assumption : a **uniform** flow.

# How is actually done the measurement ?




CRESUCHIPR Team —

`https://cresuchirp.wordpress.com`

**Pulsed (temporal)**

- Fixed nozzle–detector distance
- Trigger the kinetic with a photolysis laser

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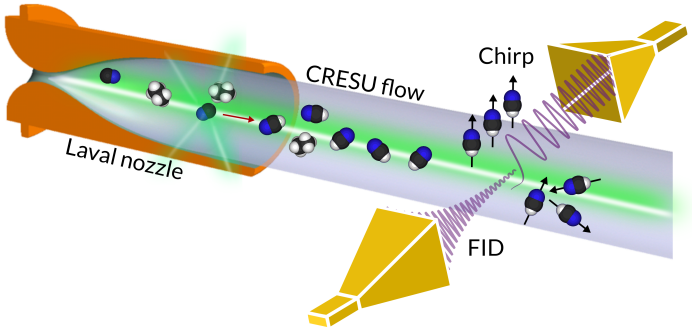


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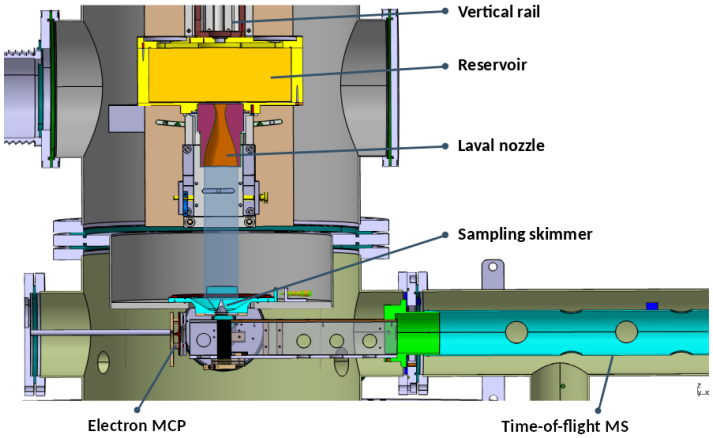



Durif et al., RSI (2021)

## Pulsed (temporal)

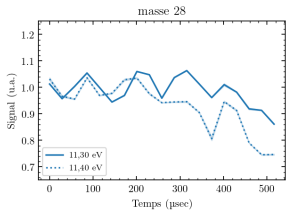
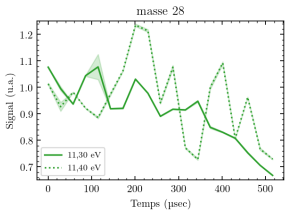
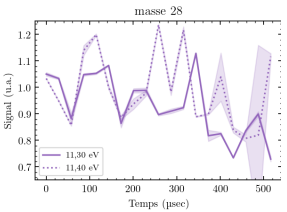
- Fixed nozzle–detector distance
- Trigger the kinetic with a photolysis laser

## Continuous (spatial)

- Nozzle–skimmer distance is varied
- Steady-state signal along the flow axis

# A kinetic trace : the continuous scheme

$$HCOOH + HCOOH \longrightarrow (HCOOH)_2$$

| **HCOOH** | **0.29 %** | **0.86 %** | **1.45 %** |
|---|---|---|---|
| **N2+** |  |  |  |

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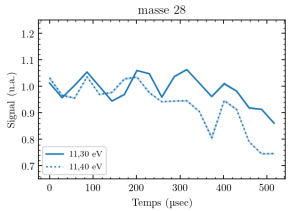
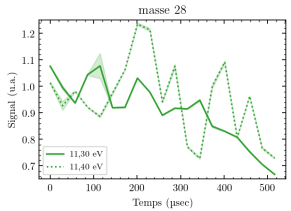
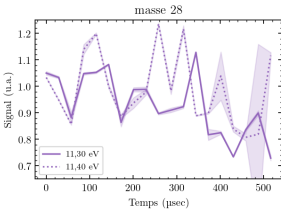
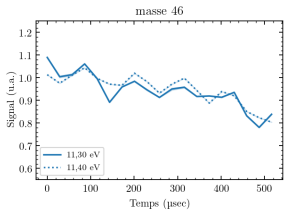
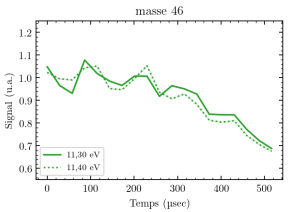
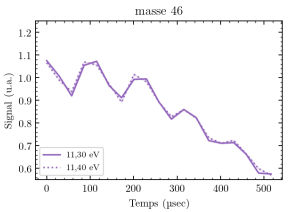
| **N2+** |  |  |  |
| **HCOOH+** |  |  |  |

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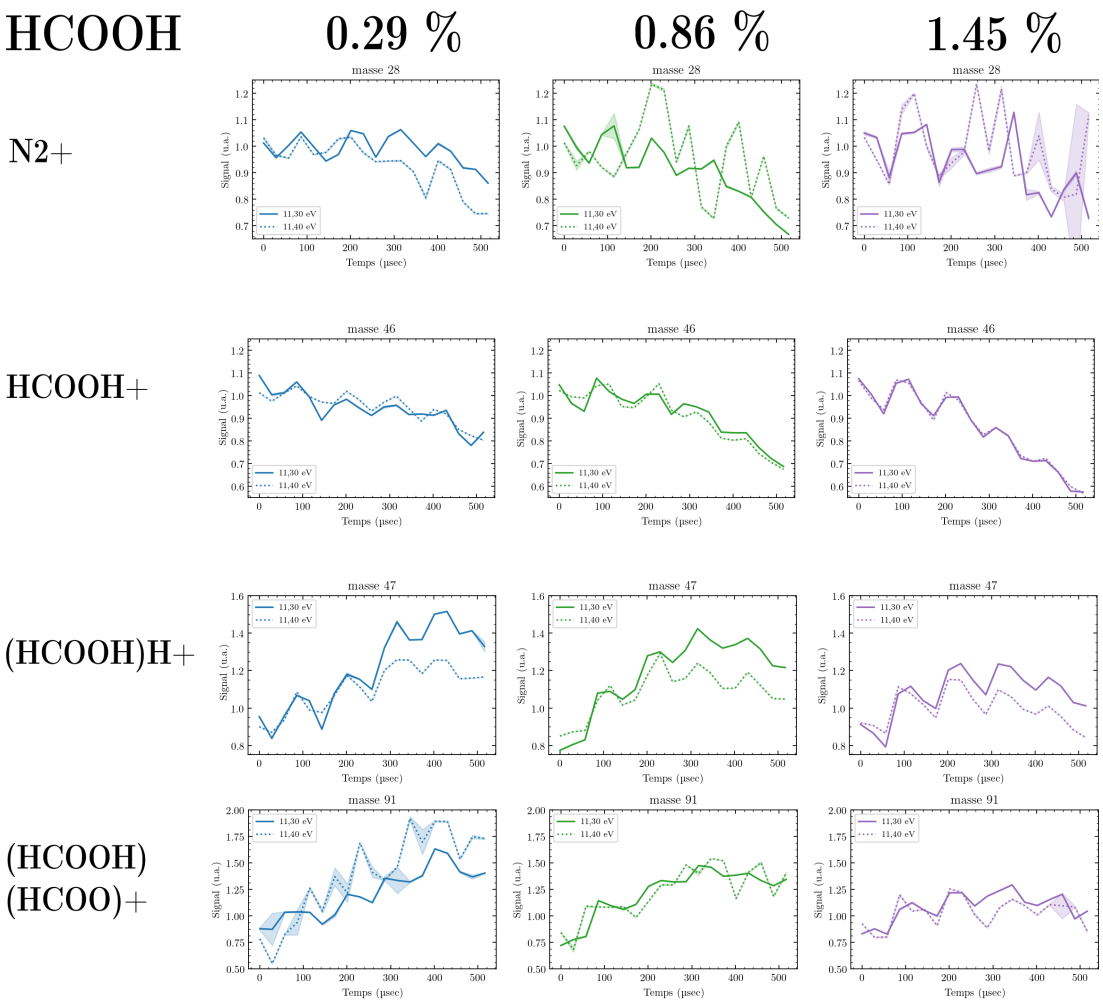
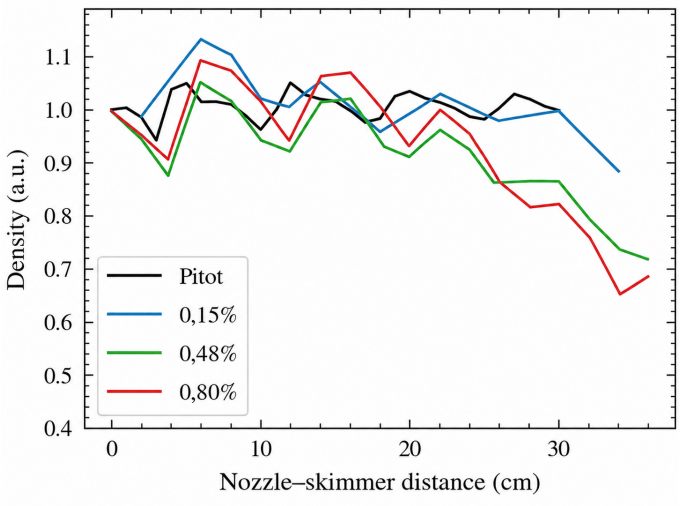
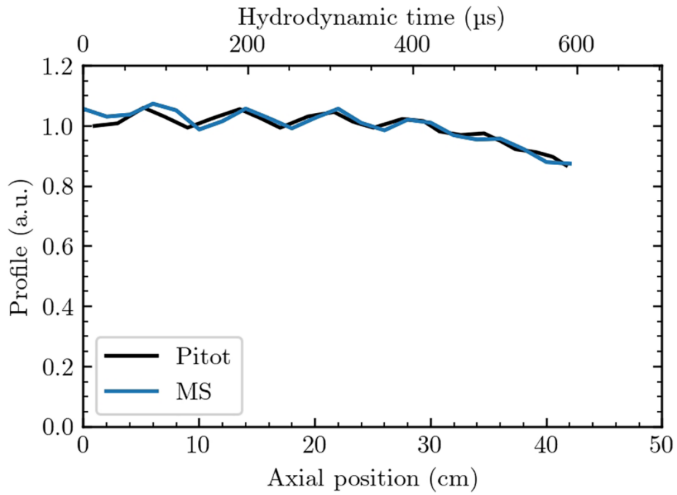



Durif's Ph.D. thesis, 2019.

# My understanding : what the signal really reflects




Durif.s Ph.D. Thesis, 2019.



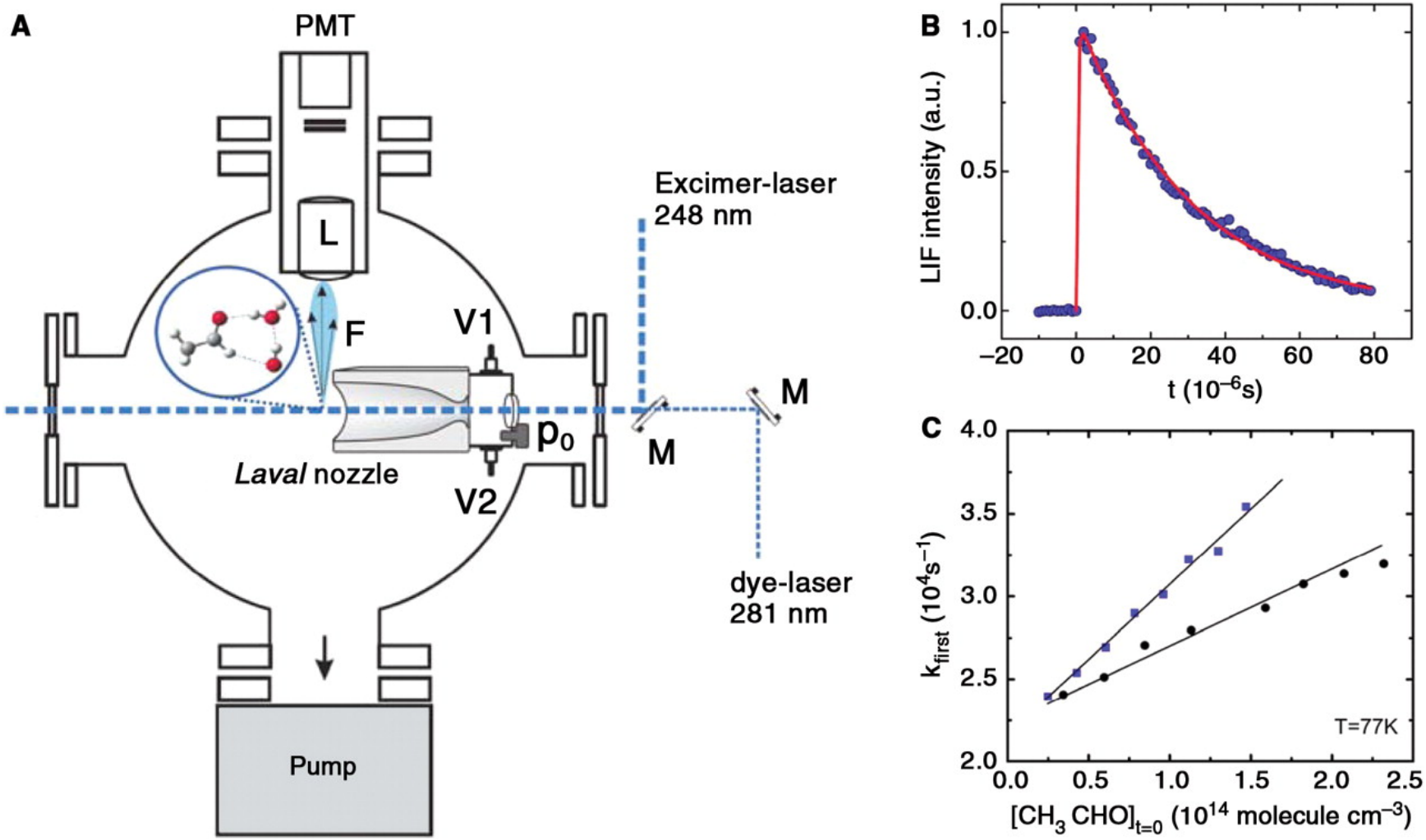

Durif, Physics of Fluids, 2022.

Results are driven by diffusion, not by chemical reactions !

Reagent concentration increase $\propto$ Temperature increase $\Rightarrow$ Flow density drop.

For the comprehensive analysis $\Rightarrow$ arXiv:2306.12349 (Durif, 2023)

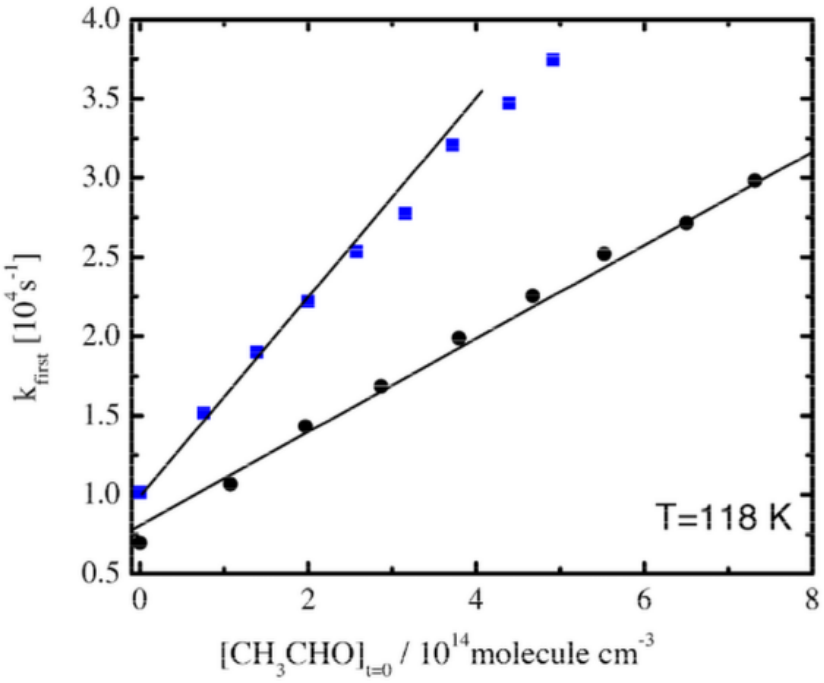
# Pulsed systems

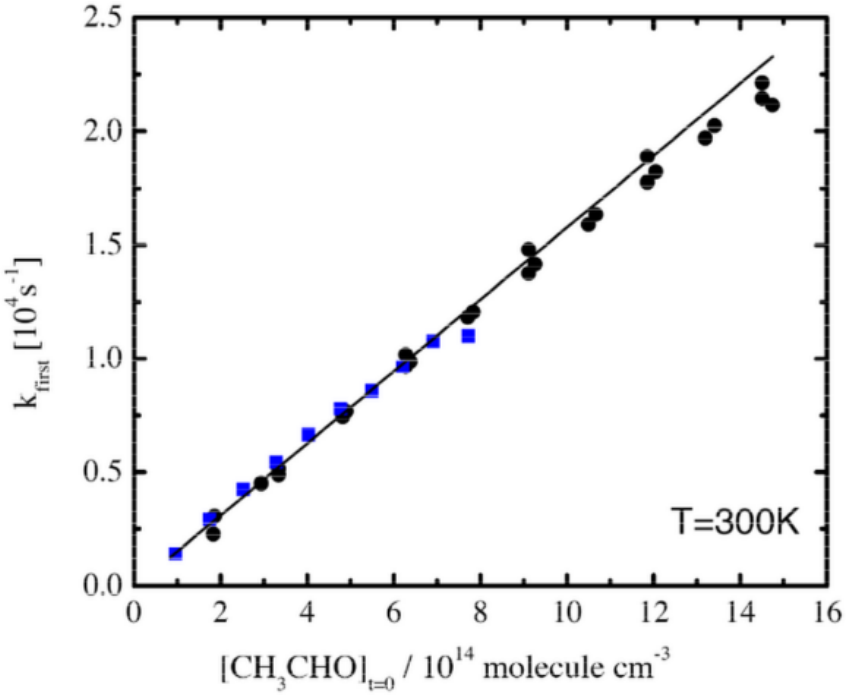



Vöhringer-Martinez et al., Science, 2007 (PLP-LIF).

# Pulsed systems

Typical data.



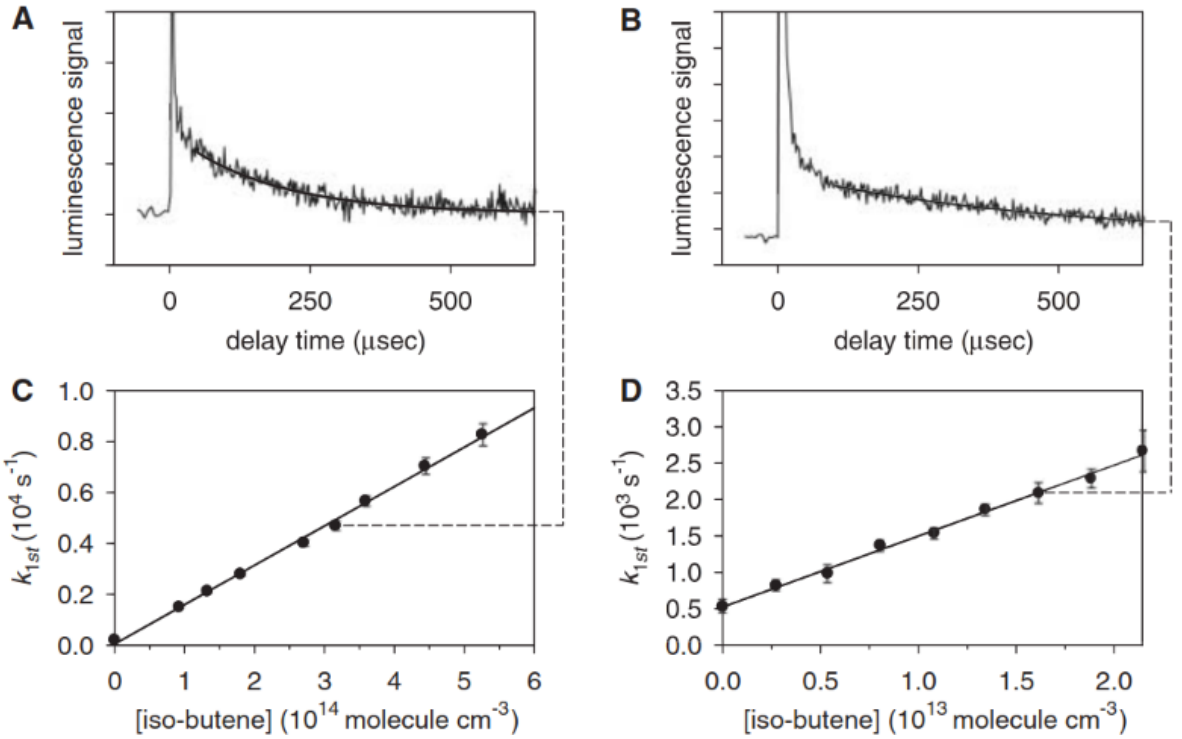




■ reaction with water ● reaction without water

Vöhringer-Martinez et al., Science, 2007, Supplementary Material.

# Pulsed systems

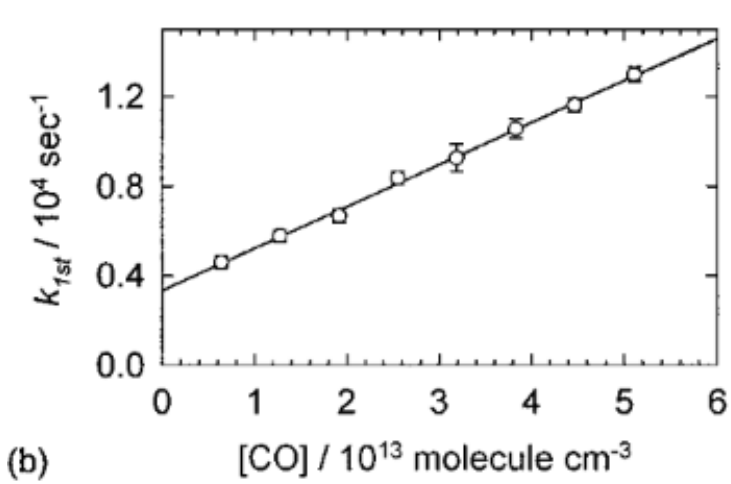
Room Temperature

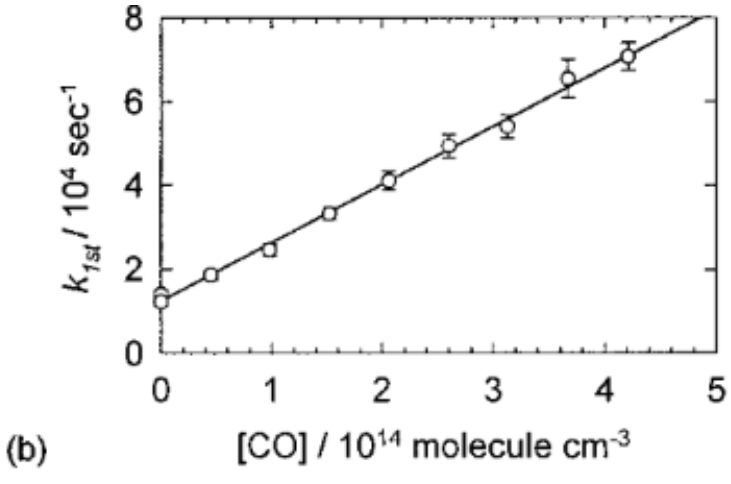



USF (cold) Temperature

Hassan et al., Science, 2007.

# Pulsed systems



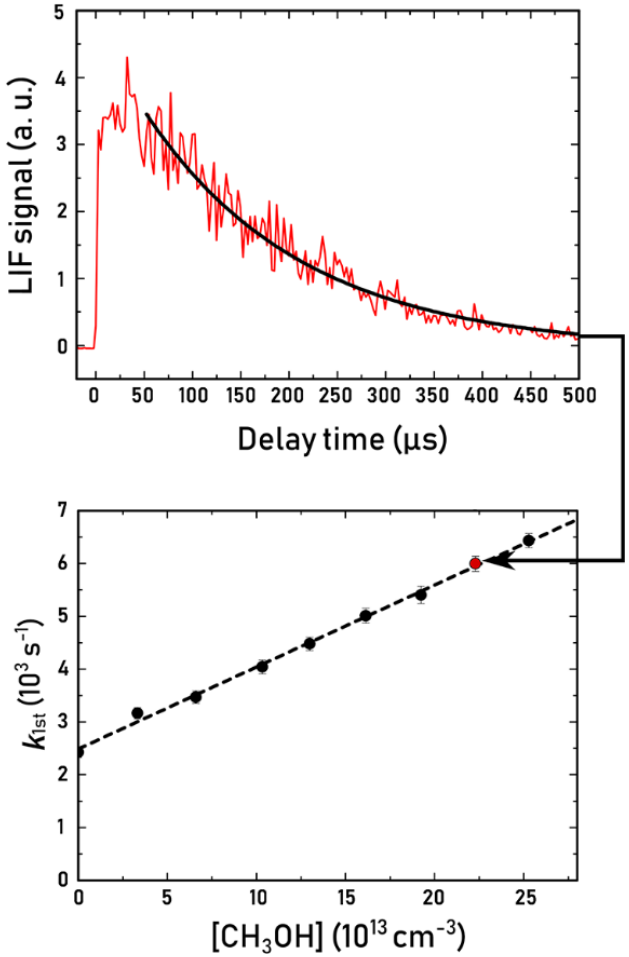




rate constants that have been obtained for removal of CH($v$=1) by CO and $N_2$ are summarized in Tables 1 and 2. The background rates, represented by the values of the intercepts in Figures 2b and 3b, are probably determined principally by reaction of CH with $CHBr_3$ and its photolysis products, possibly with some small contribution from diffusion of radicals out of the observation zone.

Herbert et al., J. Phys. Chem., 1996.

# Pulsed systems

laser scatter. The nonzero intercept in the second order plot, shown in the lower panel of Figure 2, is due to the loss of CN by diffusion out of the probed beam area and by reaction with the precursor and/or impurities in the buffer gas. As the laser alignment and other external factors may change over periods of days, the intercepts of different second-order plots are not necessarily constant. Therefore, we derive the second-order




Gupta et al., J. Phys. Chem. A, 2019.

# Early uniform-flow kinetics : Rowe et al., 1989

and the length that the ions have to travel through before reaching the reaction zone. 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

Rowe et al., J. Chem. Soc., Faraday Trans. 2, 1989.

# Another look : Chirped pulse spectroscopy

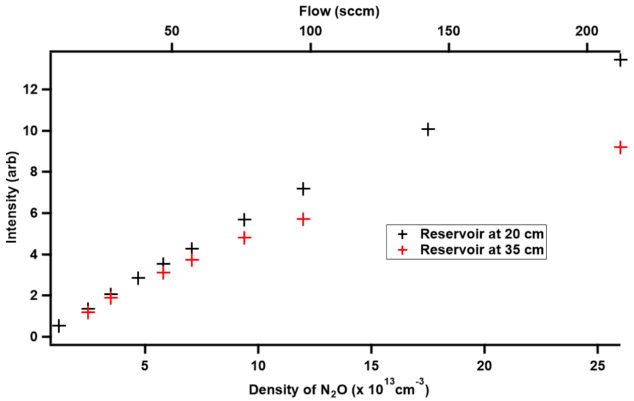



Figure 18: Clustering test in the Ar 30 K nozzle using $N_2O$ $J$ = 3-0 transition.

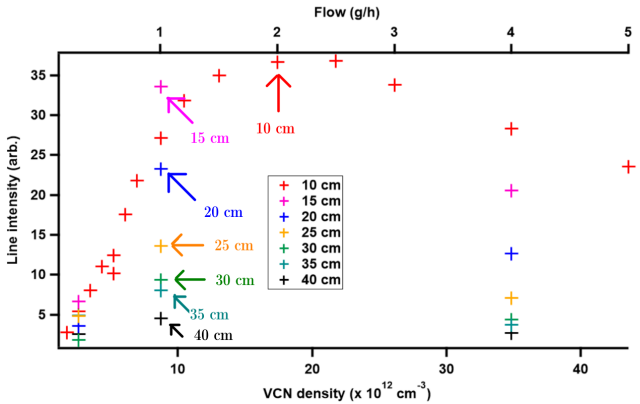
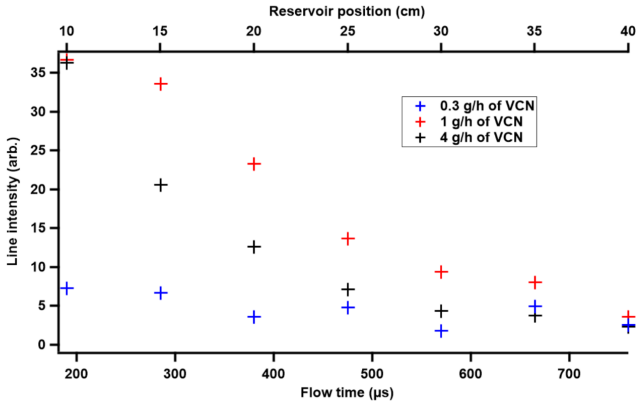



Figure 19: Clustering test in the Ar 30 K nozzle using acrylonitrile $J_{Ka,Kc}$ = $8_{0,8}$-$7_{0,8}$ transition




Guillaume, Appendix at Ph.D. Thesis (2021)

# Another look : PLP-LIF + OFC

being well-characterized by a single temperature. It is, therefore, unclear why there is a discrepancy between the molecular rotational temperature of a stable species within the USF and the Pitot impact pressure measurements, and a further detailed investigation would be desirable. It should be noted that this same nozzle is used in

**TABLE III.** A summary of the flow temperatures obtained from impact pressure measurements and spectroscopic analysis.

| Method | Derived flow temperature/K |
|---|---|
| Impact pressure | 32(3) |
| CH LIF spectrum fitting | 40(2) |
| OCS spectrum fitting | 49.5(1) |
| Boltzmann analysis | 48.9(6) |
| Doppler temperature | ~46 |

Lucas et al., J. Chem. Phys. (2024)

# Another look : Quadrupole Mass Spectrometry

$$N^+ + C_3H_4 \longrightarrow P$$

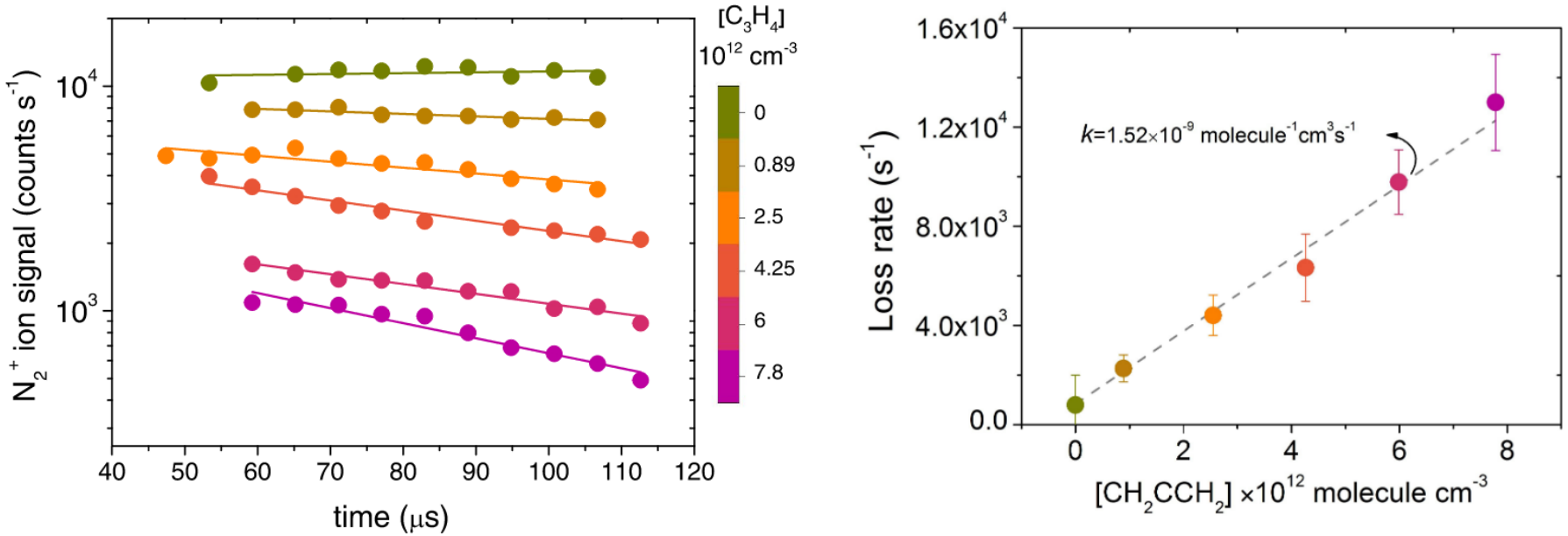



**Figure 3.** $N_2^+$ ion signal as a function of time for a range of neutral $CH_2CCH_2$ densities (left) and corresponding loss rates as a function of $CH_2CCH_2$ densities (right) at 24 K.

Mortada et al., ACS Earth Space Chem., 2022.

# Another look : Time of Flight Mass Spectrometry

$$[H_2O] + [H_2O]_n \longrightarrow [H_2O]_{n+1}$$

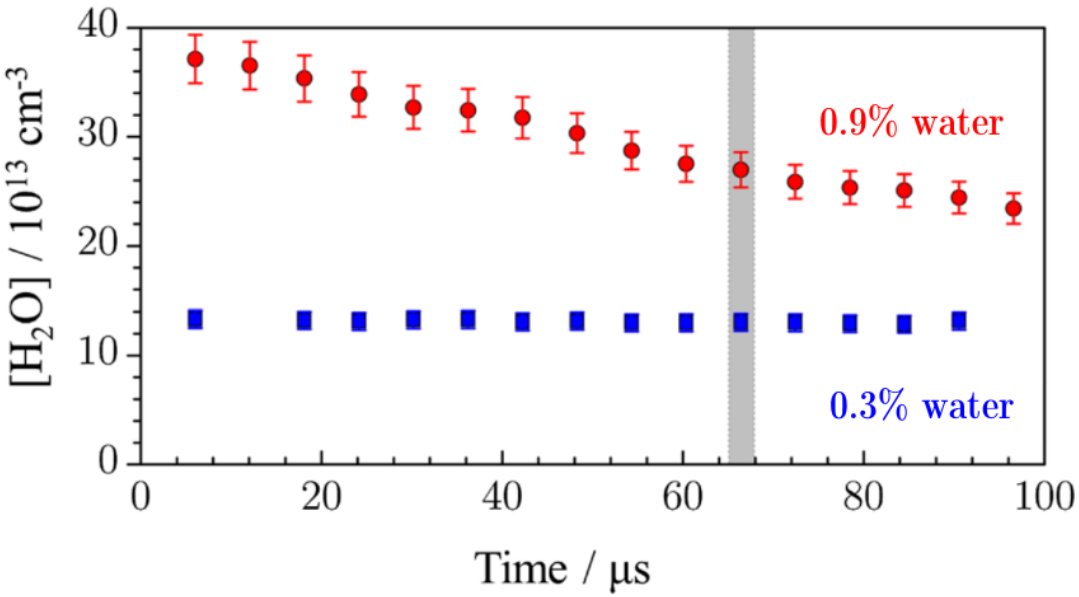



FIG. 2. Time evolution of $[H_2O]$ in the supersonic flow at 22.9 K for $[H_2O]_0$ of $13 \times 10^{13}$ cm$^{-3}$ (blue square) and $40 \times 10^{13}$ cm$^{-3}$ (red circle).

Bourgalais et al., PRL, 2016.

# Conclusion & outlook

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