

Laboratory Measurements of Gas-Phase Reactions Kinetics and Uptake on Surfaces: Application to Organic Peroxy Radical

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Marseille, July 16th 2025



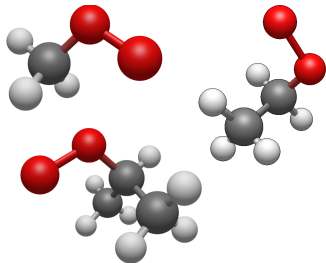
Plan

1. Context
2. Measurements
3. Results
4. Summary
5. Prospective

Context: EPHEMERAL Project

"Project EPHEMERAL has for objective to use real-time mass spectrometry to detect and speciate gas-phase organic radicals in Earth's atmosphere and other complex mixtures."

Principal investigator: Barbara Nozière.

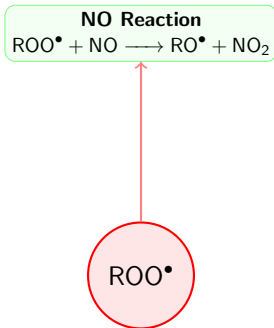


Reactivity of Organic Peroxy Radicals ($\text{ROO}^\bullet$)

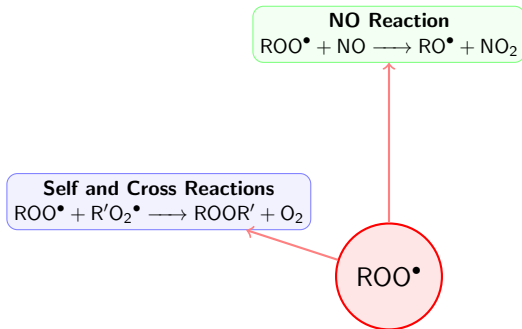
What controls $\text{ROO}^\bullet$ reactivity?



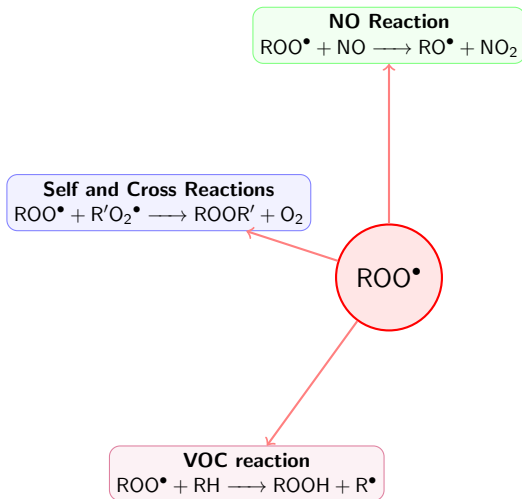
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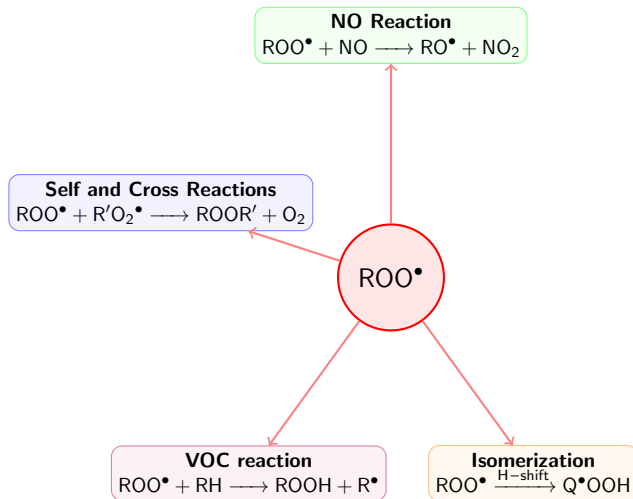
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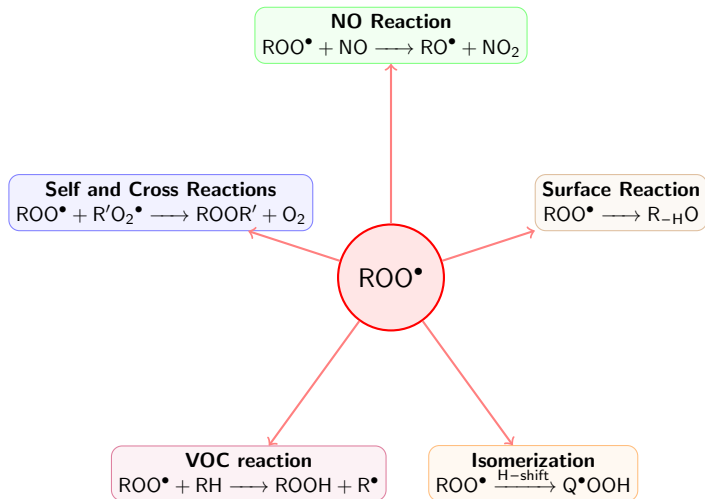
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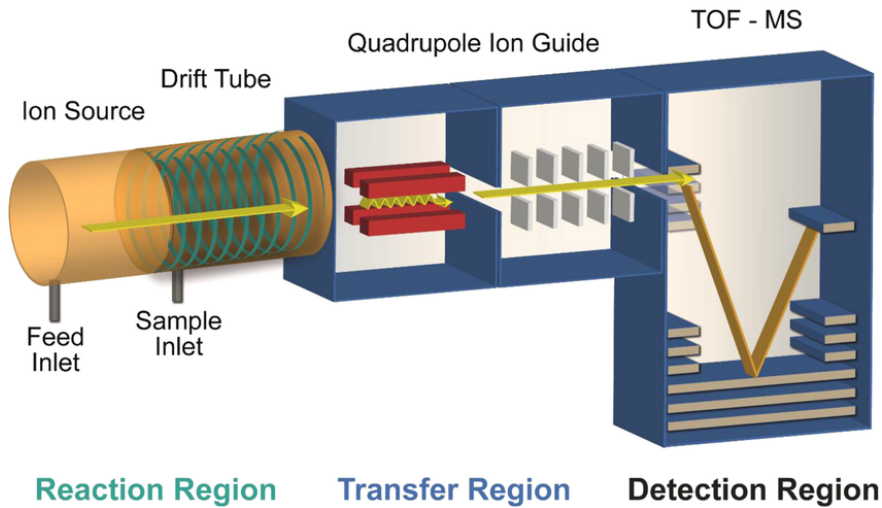
Reactivity of Organic Peroxy Radicals ($\text{ROO}^\bullet$)



Plan

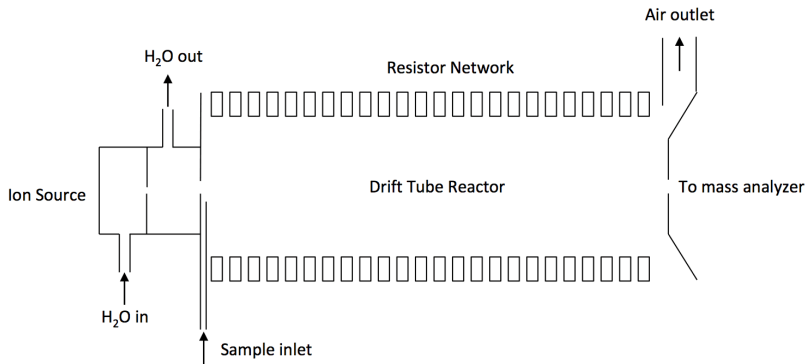
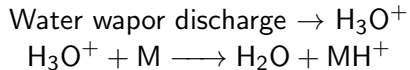
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Proton-Transfer-Reaction Mass Spectrometry

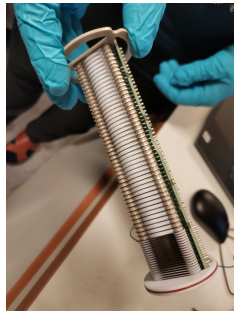
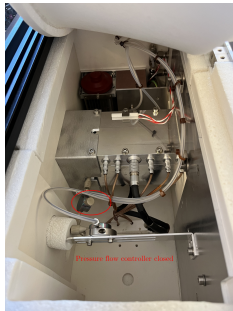


Hegen et al. 2022

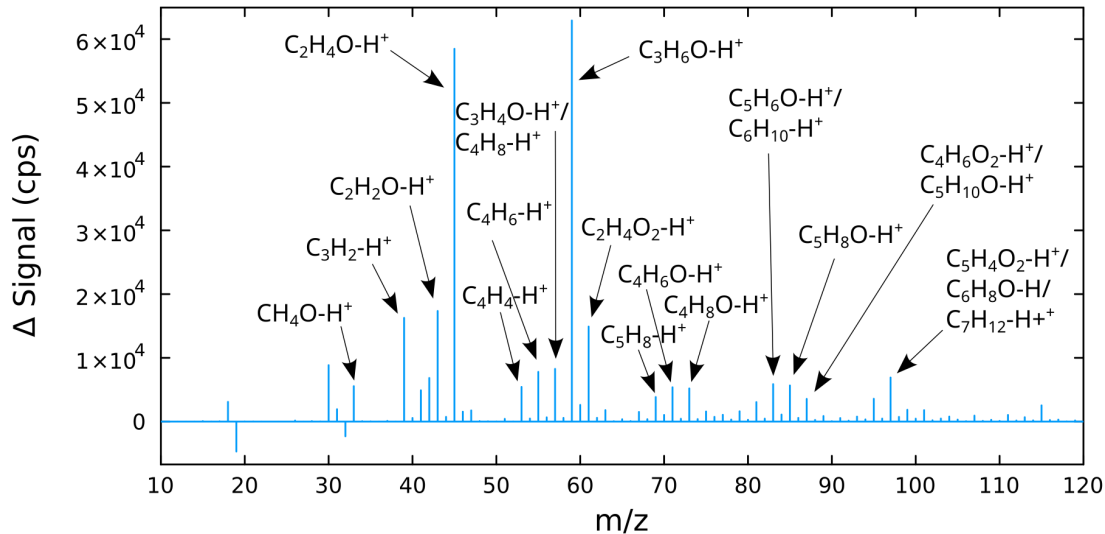
Ionisation schematic



Drift tube and chemical ionization



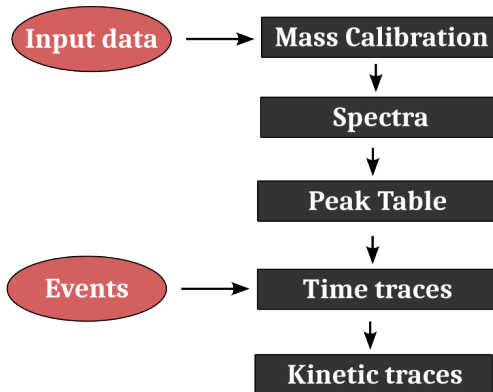
A typical mass spectrum



First task: data processing workflow



MassSpec.jl



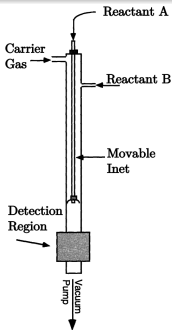
MassSpec.jl: <https://gitlab.com/odurif/MassSpec.jl>

Coupling PTR-TOF-MS with an Atmospheric Reactor

Cylindrical reactor (usually glass/Pyrex) with laminar flow (1-10 m/s) allowing kinetic control.

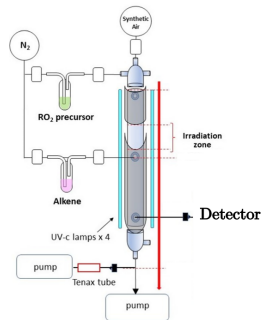
Injector

- Movable inlet for reactant introduction
- Controls reaction initiation point
- Radicals often injected
- Adjustable position → variable reaction time

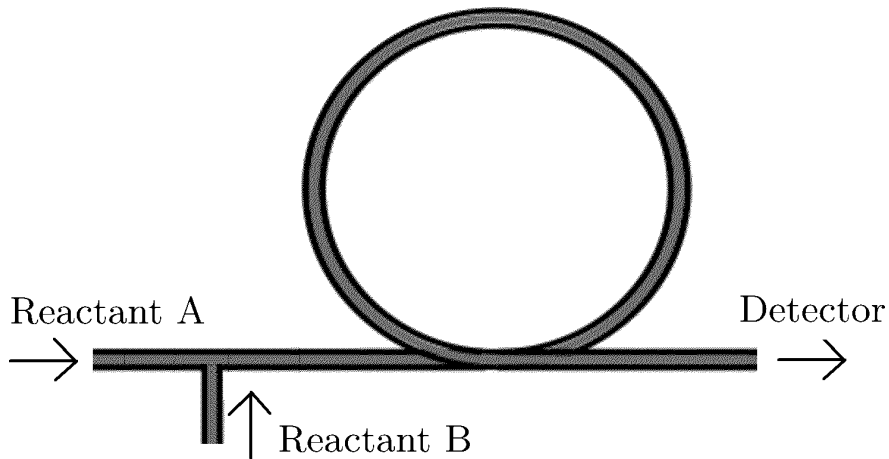


Movable photolysis window

- UV-transparent tube (quartz)
- Continuous photolysis (UV lamps)
- Radicals produced in-situ
- Adjustable photolysis zone

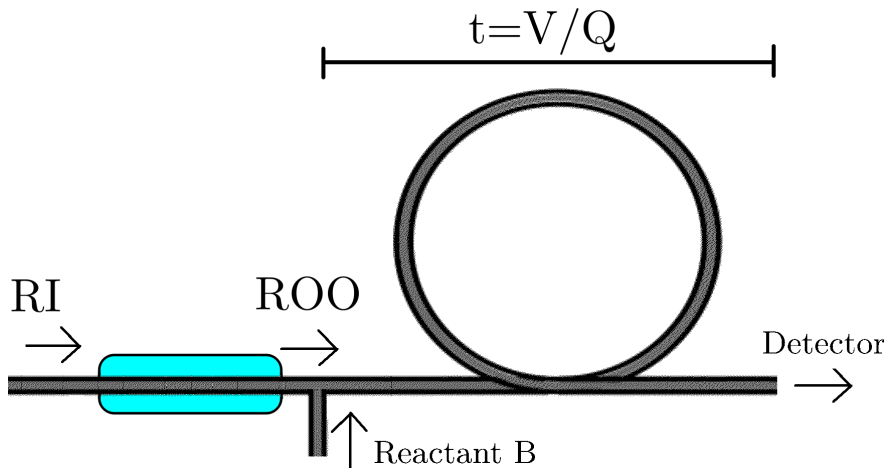


A Simple Flow Tube for Chemical Kinetics



Simply what we need for chemical kinetics.

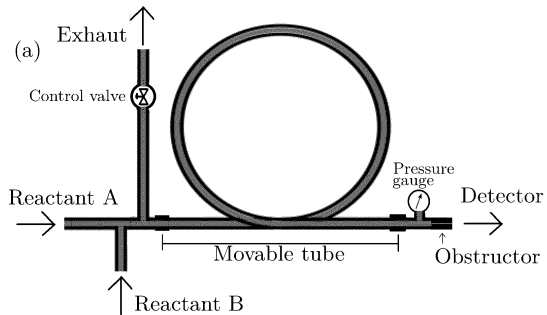
A Simple Flow Tube for Chemical Kinetics



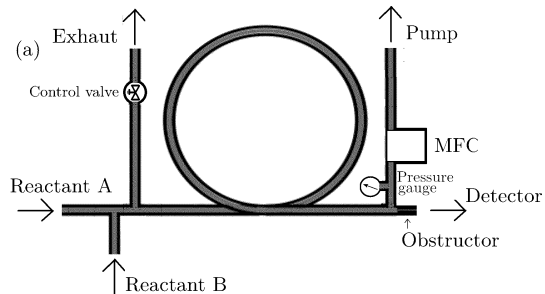
Simply what we need for chemical kinetics of organic peroxy radicals.

Flow Tube Variant

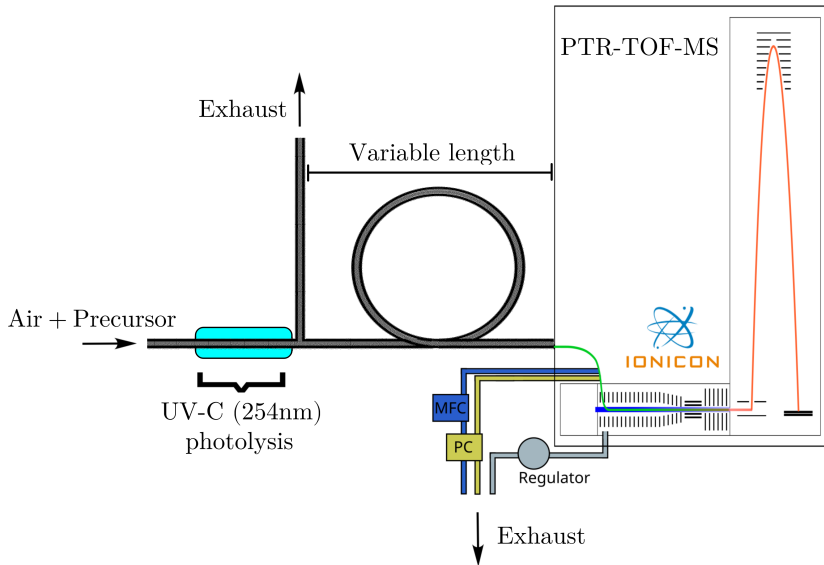
Varying the tube length



Varying the reactor flow (no mechanical parts)



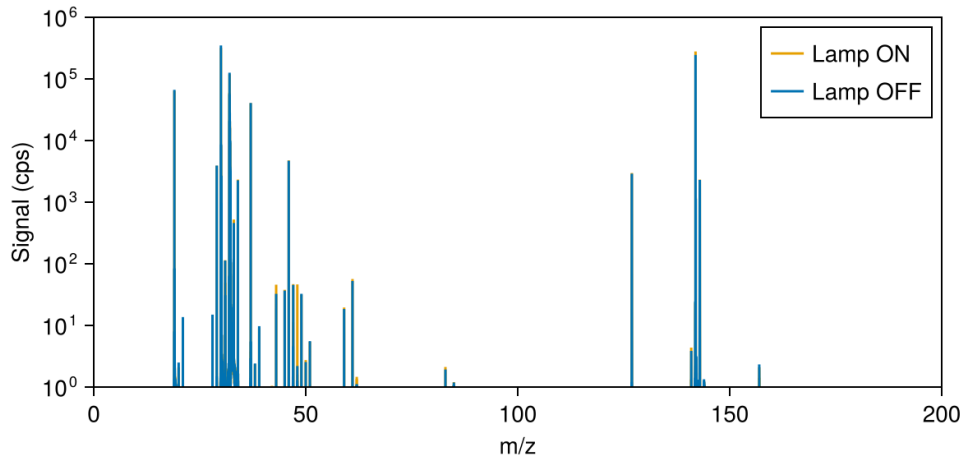
The Coupling with a PTR-TOF-MS



Plan

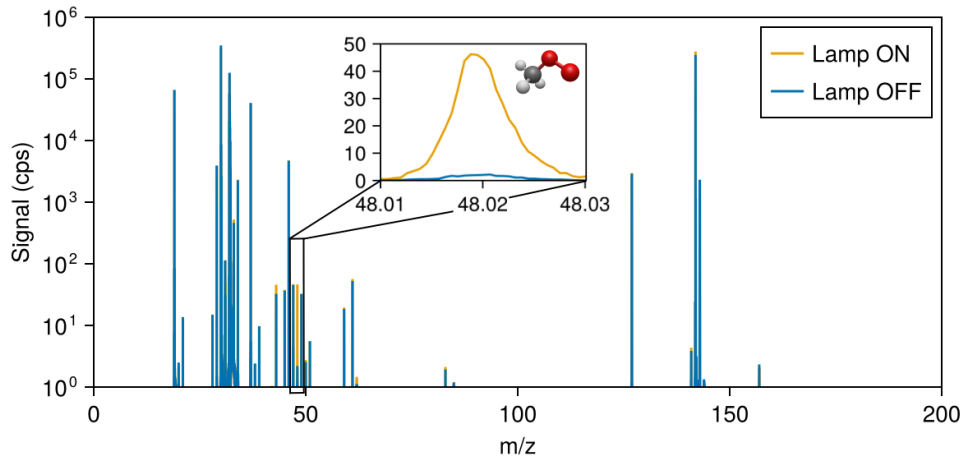
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Peroxy radicals detection



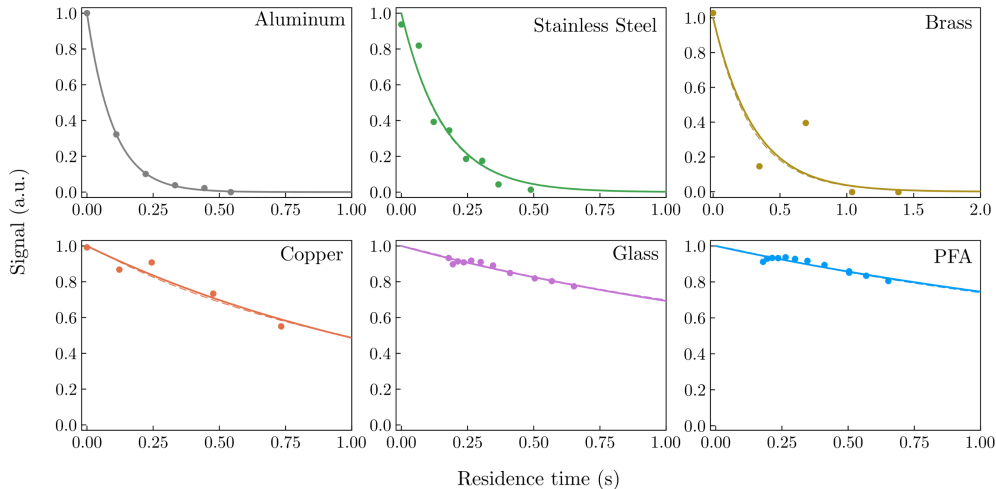
Typical mass spectrum recorded for one kinetic point.

Peroxy radicals detection



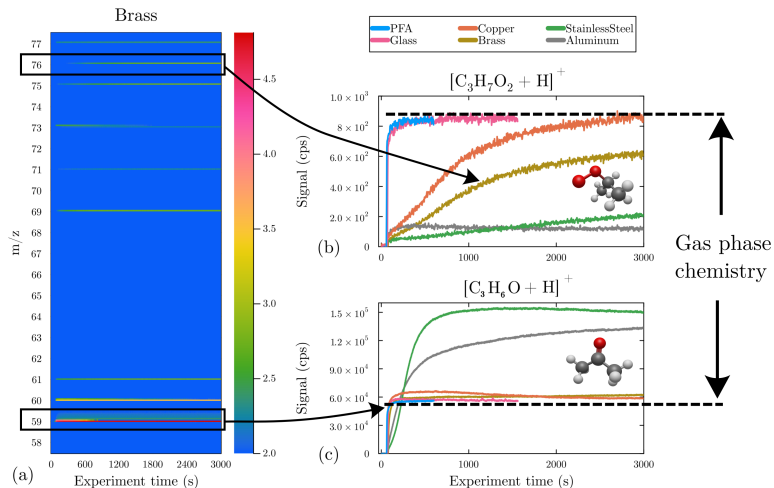
Direct detection of $\text{CH}_3\text{OO}^\bullet$ at ppb sensitivity.

Kinetics: uptake on Walls



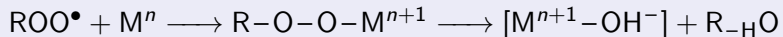
Kinetics measurements using different reactor materials.

Uptake on Walls



Durif et al, 2024 (JACS Au), DOI:10.1021/jacsau.4c00060
Dataset, DOI: 10.5281/zenodo.10790197

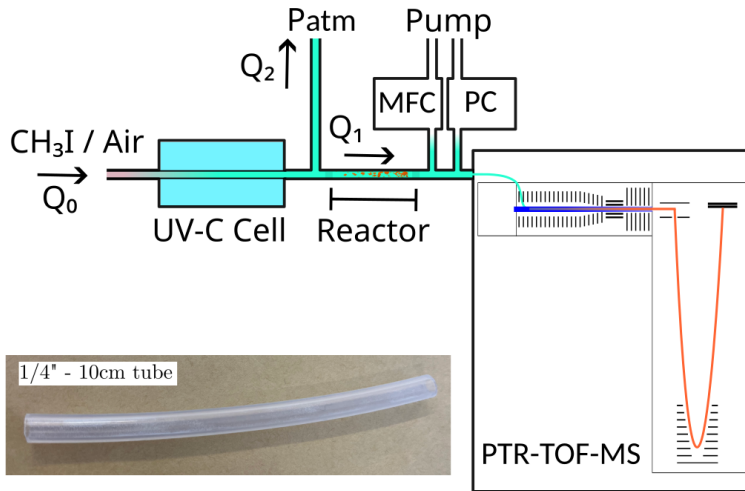
- Strong ROO•-Metals interactions.
- PFA walls do not affect (at least not directly) RO₂ chemistry (!).
Recommended uptake: 0.



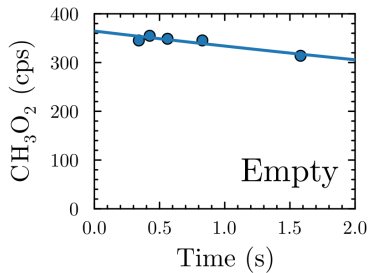
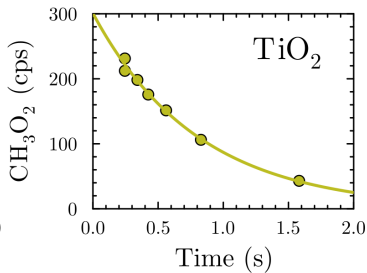
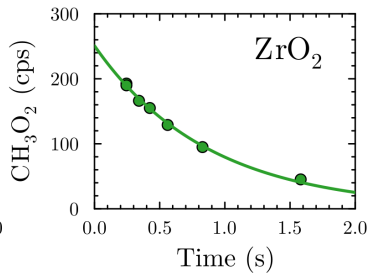
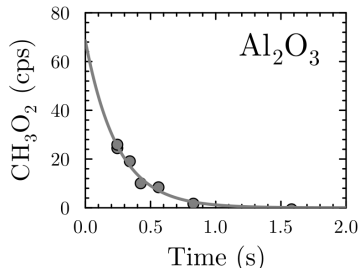
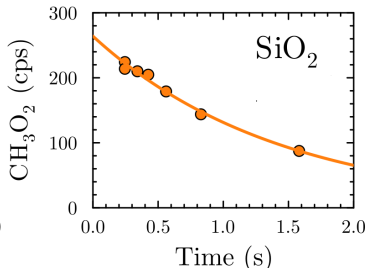
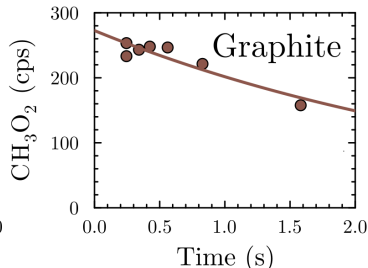
Next question

How to quantify uptake by atmospherically relevant materials?

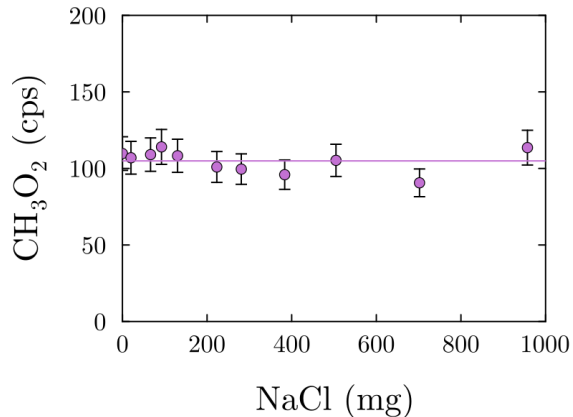
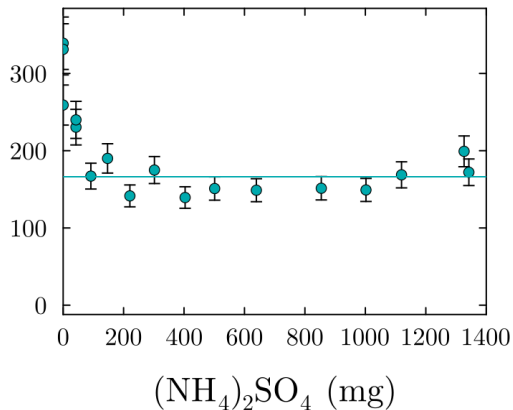
Versatile Setup for Measuring Uptake on Surfaces



Uptake on surfaces

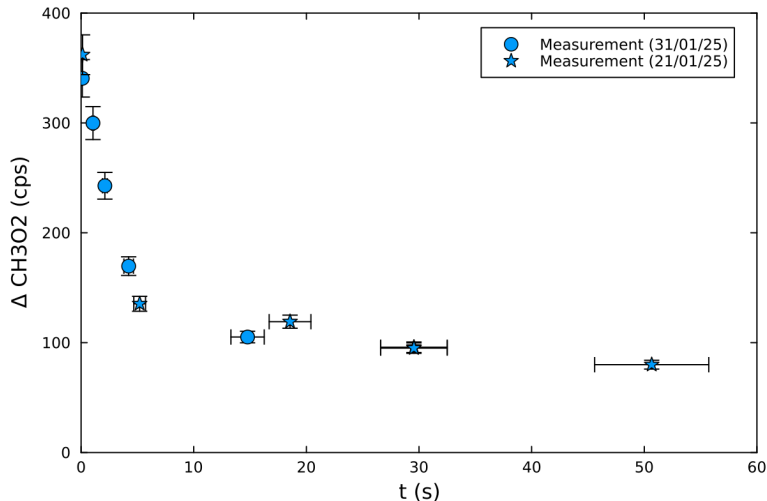


No Uptake on Dry Salts



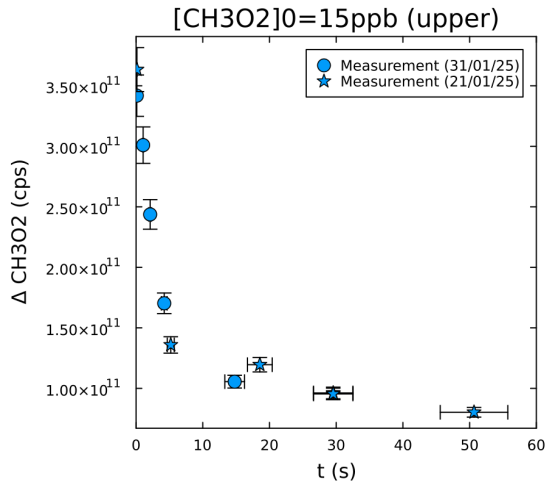
The CH_3O_2 mystery

Self-reaction: finding strong discrepancies. What is really reliable?

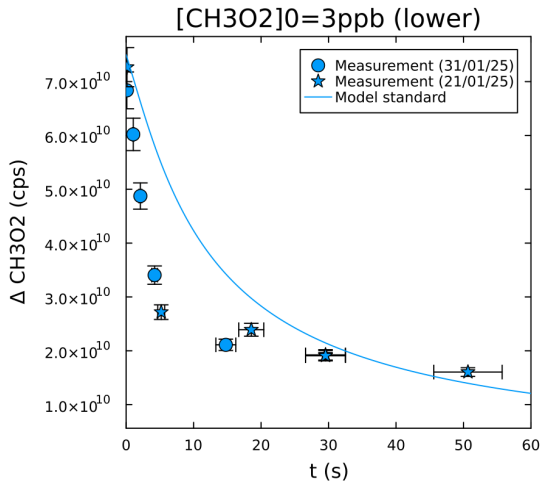
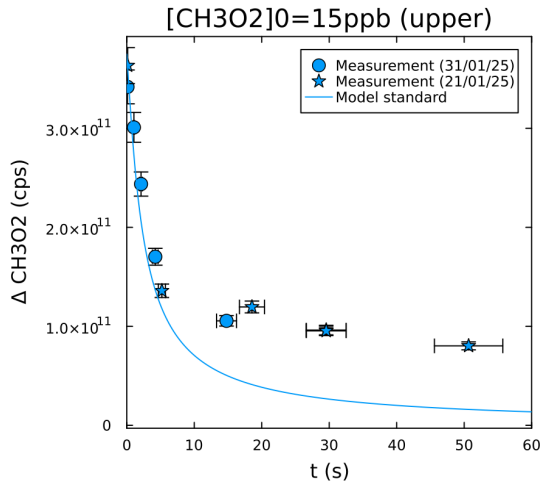


- $[\text{CH}_3\text{I}] = 2.1$ ppm.
- Titration: $[\text{NO}_2] = 30$ ppb with large NO excess $\Rightarrow$ assuming 15 ppb of $[\text{CH}_3\text{O}_2]_0$ (probably upper case).

The CH_3O_2 mystery

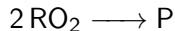


The CH_3O_2 mystery



Fitting a system

Considering only the self reaction

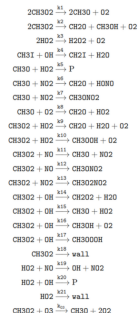


$$\frac{d[\text{RO}_2]}{dt} = -2 k [\text{RO}_2]^2$$

Analytical solution:

$$[\text{RO}_2](t) = \frac{1}{\frac{1}{[\text{RO}_2]_0} + 2 k t}$$

Considering a whole chemical system



Catalyst.jl: a modern solver

How to fit these data (i.e. adjust k parameters) when using a reaction set?

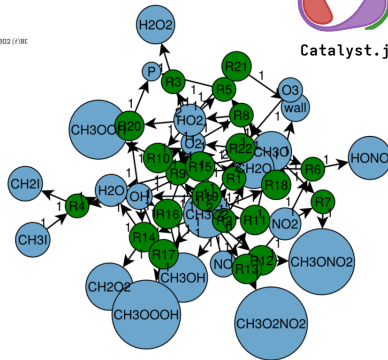
```

dCH3O2(t) = -k18CH3O2(t) - (CH3O2(t))^3k1 - k10CH3O2(t)H2O(t) - k11CH3O2(t)H2O(t) - k12CH3O2(t)H2O(t) - k13CH3O2(t)H2O(t) - k14CH3O2(t)OH(t) - k15CH3O2(t)OH(t) - k16CH3O2(t)OH(t) - k17CH
dCH3O(t) = -(CH3O2(t))^3k1 + k11CH3O2(t)H2O(t) + k15CH3O2(t)H2O(t) - k5CH3O(t)CH3O(t) - k6H2O(t)CH3O(t) - k7H2O(t)CH3O(t) - k8CH3O(t)O2(t) + k_03CH3O2(t)O3(t)
dO2(t) = 1/2(CH3O2(t))^3k1 + k10CH3O2(t)H2O(t) + k16CH3O2(t)OH(t) + 1/2(CH3O2(t))^3k2 + 1/2(H2O(t))^3k3 - k8CH3O(t)O2(t) + k9CH3O2(t)H2O(t) + 2k_03CH3O2(t)O3(t)
dCH2O(t) = 1/2(CH3O2(t))^3k2 + k6H2O(t)CH3O(t) + k8CH3O(t)O2(t) + k9CH3O2(t)H2O(t)
dCH3OH(t) = k16CH3O2(t)OH(t) + 1/2(CH3O2(t))^3k2
dH2O(t) = -k21H2O(t) - k10CH3O2(t)H2O(t) + k15CH3O2(t)OH(t) - k19H2O(t)H2O(t) - k20OH(t)H2O(t) - (H2O(t))^3k3 - k5CH3O(t)H2O(t) + k8CH3O(t)O2(t) - k9CH3O2(t)H2O(t)
dH2O2(t) = 1/2(H2O(t))^3k3
dCH3I(t) = -k4OH(t)CH3I(t)
dOH(t) = -k14CH3O2(t)OH(t) - k15CH3O2(t)OH(t) - k16CH3O2(t)OH(t) - k17CH3O2(t)OH(t) + k19H2O(t)H2O(t) - k20OH(t)H2O(t) - k4OH(t)CH3I(t)
dCH2I(t) = k4OH(t)CH3I(t)
dH2O(t) = k14CH3O2(t)OH(t) + k4OH(t)CH3I(t) + k9CH3O2(t)H2O(t)
dP(t) = k20OH(t)H2O(t) + k5CH3O(t)H2O(t)
dNO2(t) = k11CH3O2(t)H2O(t) - k13CH3O2(t)H2O(t) + k19H2O(t)H2O(t) - k6H2O(t)CH3O(t) - k7H2O(t)CH3O(t)
dHONO(t) = k6H2O(t)CH3O(t)
dCH3ONO2(t) = k12CH3O2(t)H2O(t) + k7H2O(t)CH3O(t)
dCH3OOH(t) = k10CH3O2(t)H2O(t)
dNO(t) = -k11CH3O2(t)H2O(t) - k12CH3O2(t)H2O(t) - k19H2O(t)H2O(t)
dCH2O2(t) = k13CH3O2(t)H2O(t)
dCH2O2(t) = k14CH3O2(t)OH(t)
dCH3OOH(t) = k17CH3O2(t)OH(t)
dval1(t) = k18CH3O2(t) + k21H2O(t)
dO3(t) = -k_03CH3O2(t)O3(t)

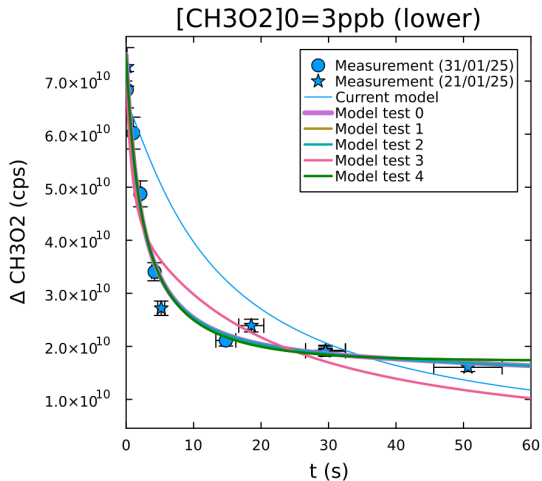
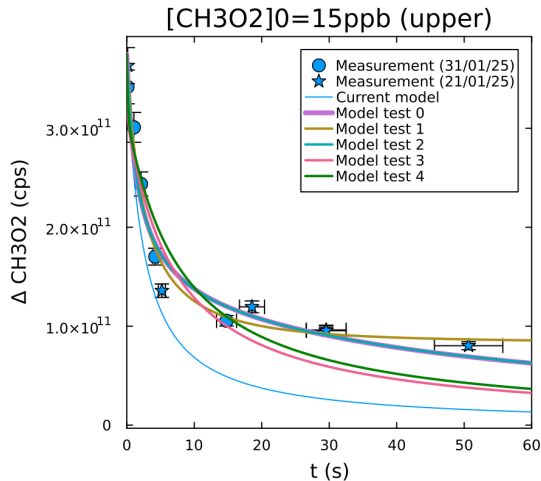
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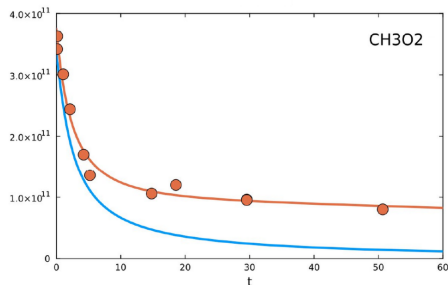
Catalyst.jl



The CH_3O_2 mystery



My result for CH₃O₂ self-reaction



	previous	fit
$2 \text{ CH}_3\text{O}_2 \rightarrow 2 \text{ CH}_3\text{O} + \text{O}_2$	2.20e-13	7.90e-15
$2 \text{ CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{OH} + \text{CH}_2\text{O} + \text{O}_2$	1.1e-13	3.83e-15
$2 \text{ CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2$	1.75e-14	6.18e-16
$\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2$	5.20e-12	
$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2$	2.00e-15	
$\text{CH}_3\text{O}_2 + \text{I} \rightarrow \text{CH}_3\text{O}_2\text{I}$	2.00e-12	8.07e-13
$\text{CH}_3\text{O}_2\text{I} + \text{I} \rightarrow \text{CH}_3\text{O}_2 + \text{I}_2$	1.50e-11	1.22e-13
$2 \text{ HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	1.60e-12	
$\text{HO}_2 + \text{I} \rightarrow \text{HO}_2\text{I}$	2.00e-11	
$\text{HO}_2\text{I} + \text{I} \rightarrow \text{HO}_2 + \text{I}_2$	1.50e-10	
$\text{CH}_3\text{O}_2 \rightarrow \text{walls}$	3.00e-03	0.00e+00
$\text{HO}_2 \rightarrow \text{walls}$	3.00e-03	
$2 \text{ I} \rightarrow \text{I}_2$	1.00e-15	

Results indicates the CH₃O₂ self reaction rate constant is one order of magnitude slower than the value reported in the IUPAC.

Note: Onel et al. (2022) reported a CH₃O₂ self reaction value 30 % slower than the IUPAC recommendation (FAGE instrument).

Summary

- A spectrometer detecting unambiguously CH_3O_2 at a ppb sensitivity.
- Versatile flow tube approach: applicable for gas-phase reaction but also gas-liquid and gas-surface uptake.
- Simple 1/4" tubing, no gas-mixing issues, easy-to-build, easy-to-use, robust, cost-less, precise.
- Strong RO_2 uptake on metals and metals oxides.
- PFA, glass and dry salts are founds inert toward RO_2 .
- Slow CH_3O_2 self-reaction.
- In low- NO_x environments (e.g., clean air, forests), RO_2 chemistry could shifts from NO-dominated pathways to surface-mediated processes (aerosols, water).
- A complete framework for PTR-MS data processing and kinetics analysis: `MassSpec.jl`.

Prospective: The $\text{ROO}^\bullet$ – H_2O Enigma

Water dramatically impacts $\text{ROO}^\bullet$ reactivity

- Current models cannot explain this effect.
- PERCA: problem managed with an unsatisfactory tip “RH-dependent wall losses”.

Proposition:

Direct detection of $\text{ROO}^\bullet$ – H_2O complexes
by coupling such flow tube reactor to **i2PEPICO @ SOLEIL**.

Acknowledgments

EPHEMERAL Project

Pr. Barbara Nozière
Principal Investigator

Collaborators:

- ▶ Sébastien Dusanter
- ▶ Felix Piel
- ▶ Armin Wisthaler

PhD Candidates & Post-docs:

- ▶ Lauren Cork
- ▶ Clara Strunz
- ▶ Juana Salas



Thank you

Looking for a postdoc!