

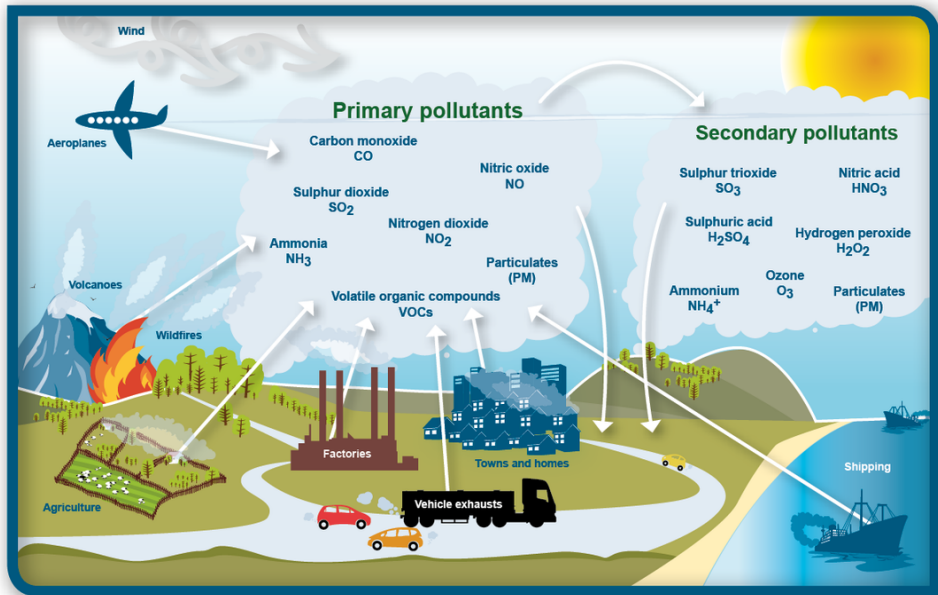
Gas-Phase Tracking of Molecules by Proton-Transfer-Reaction Mass Spectrometry: Application to Atmospheric Chemistry

Olivier Durif

Department of Chemistry, KTH Royal Institute of Technology, Stockholm, Sweden

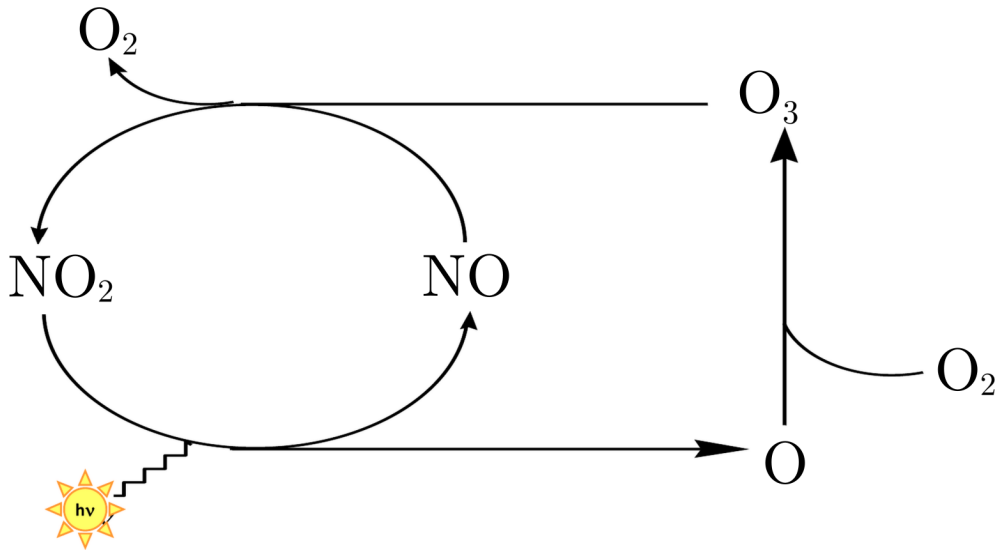
KTH, Stockholm, 6th May 2025



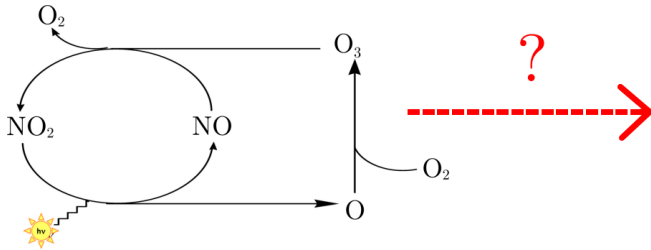


Credit: mrgscience.com

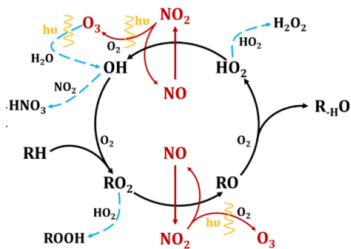
Leighton cycle, 1961



Connexion between ozone and smog



A chemistry governed by free radicals



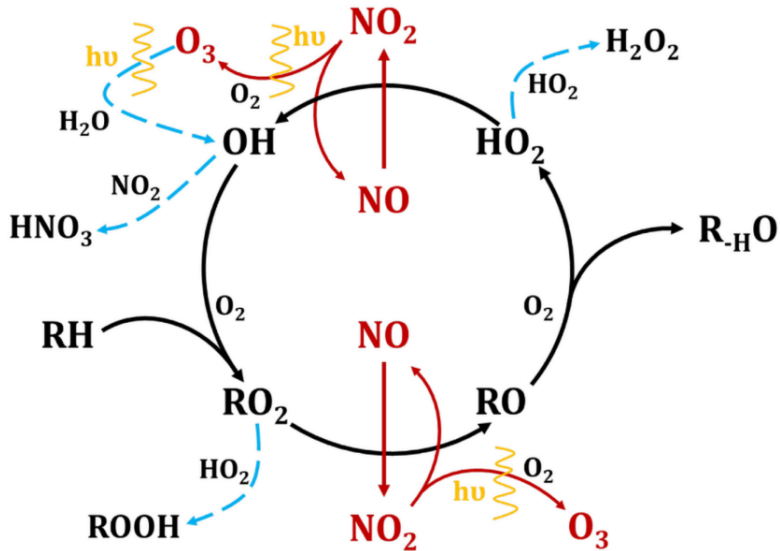
Fowler et al., 1999

VOCs/HOMs
----->
Aerosols



VOCs complicate atmospheric chemistry a lot.

Leighton cycle and VOCs



Fowler et al., 1999

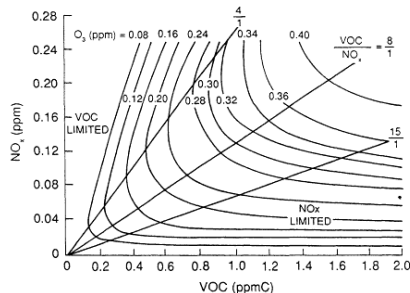
Regulated Pollutants and Modeling Tools

Primary Regulated Pollutants

O₃, NO_x (NO + NO₂), PM_{2.5}/PM₁₀, CO, SO₂.

Modeling Tools

- EKMA (Empirical Kinetic Modeling Approach)
 - Simple model: About 20 reactions (VOC/NO_x → O₃)
 - E.g. OZIPM (Ozone Isopleth Plotting Mechanism)
- MCM (Master Chemical Mechanism)
 - 17k+ explicit reactions involving 6k species.
 - Use for targeted simulations.
 - AtChem2, F0AM, Cantera, JIBox, ...
- Complete Chemical Transport Model
 - Predict air quality at regional/global scales by simulating atmospheric chemistry, emissions, transport, deposition, etc
 - CMAQ, GEOS-Chem, LOTOS-EUROS, ...



Classic EKMA isopleth diagram: ozone production as a function of NO_x and VOC emissions. Dodge (1977).

Measuring Gas Traces: O₃ and NO_x

A multitude of well-established techniques and reference dataset.

Many Instrumental Methods

Ozone (O₃)

- UV Spectrophotometry (253.7 nm) (Ground measurements)
- Brewer/Dobson (Stratospheric measurements)
- Chemiluminescence
- IR Spectroscopy (Satellite remote sensing)

NO_x

- CAPS for NO₂ (Cavity Attenuated Phase Shift, 450 nm)
- LIF for NO (UV Laser-Induced Fluorescence)
- Chemiluminescence + Photolytic Converter (NO + O₃ and NO₂ → NO)
- Electrochemical Sensors (Low-cost networks)
- DOAS (Differential Optical Absorption Spectroscopy)

Many Reference Data

Long-term trends

- Ground stations
 - Atmospheric research observatories (~ 30 worldwide)
 - Air quality networks (e.g. Stockholm: SLB-analys)
 - Estimate: >15k to 20k reference stations worldwide.
 - Long-term records and regulatory monitoring.
- Satellites
 - TROPOMI (ESA), OMI (NASA), TEMPO (NASA), FY (CNSA), ...
 - Several dozen satellites, monitoring O₃ and NO_x among others (CO₂, SO₂, CH₄, aerosols, ...).

Ponctual measurements

- Numerous data by baloon and aircraft
- Numerous data from field campaigns

Measuring Gas Traces: OH, RO, RO₂ and HO₂

Techniques for Short-Lived Radicals

Chemical Ionization Mass Spectrometry (CIMS)

- OH (indirect, with SO₂)
- HO₂ (with reagent-specific methods: Br-CIMS, PerCIMS)
- RO₂ (direct detection by proton-transfer-reaction)

Laser-Induced Fluorescence (LIF, 308 nm)

- OH (direct detection)
- HO₂ + RO₂ (indirect, OH measured via chemical conversion:
 $\text{HO}_2 + \text{NO} \longrightarrow \text{OH} + \text{NO}_2$)
- Some RO species (limited cases)

Near/mid-IR CRDS (Cavity Ring-Down Spectroscopy) or CAPS (Cavity Attenuated Phase Shift, 450 nm)

Often:

- OH or NO₂ measurements and indirect RO₂ + HO₂ chemical conversion (PERCA: Peroxy Radical Chemical Amplification)

Few Reference Data

No commercially available ready-to-use instruments.

No long-term trends.

- Ground measurements
 - OH/HO₂: About 10 specialized labs (e.g., NOAA, MPI Mainz, Leeds).
 - RO₂: Always indirect (PERCA).
 - RO: No specific datasets.
- Satellites
 - OH/HO₂: Stratospheric/mesospheric profiles only (Aura/MLS)
 - RO/RO₂: No data

Sporadic measurements

- Some aircraft/balloons (at 30–40 km) campaigns (OH and $\sum(\text{RO}_2 + \text{HO}_2)$)
- Short-term field studies (no reference data for long-term trends)

Challenges: Short lifetimes (<1 s to minutes), low concentrations (ppq–ppt level), instrument interference, and no calibration standards.

Measuring Gas Traces: OH, RO, RO₂ and HO₂

Techniques for Short-Lived Radicals

Chemical Ionization Mass Spectrometry (CIMS)

- OH (indirect, with SO₂)
- HO₂ (with reagent-specific methods: Br-CIMS, PerCIMS)
- RO₂ (direct detection by proton-transfer-reaction)

Laser-Induced Fluorescence (LIF, 308 nm)

- OH (direct detection)
- HO₂ + RO₂ (indirect, OH measured via chemical conversion:
 $\text{HO}_2 + \text{NO} \longrightarrow \text{OH} + \text{NO}_2$)
- Some RO species (limited cases)

Near/mid-IR CRDS (Cavity Ring-Down Spectroscopy) or CAPS (Cavity Attenuated Phase Shift, 450 nm)

Often:

- OH or NO₂ measurements and indirect RO₂ + HO₂ chemical conversion (PERCA: Peroxy Radical Chemical Amplification)

Few Reference Data

No commercially available ready-to-use instruments.

No long-term trends.

- Ground measurements
 - OH/HO₂: About 10 specialized labs (e.g., NOAA, MPI Mainz, Leeds).
 - RO₂: Always indirect (PERCA).
 - RO: No specific datasets.
- Satellites
 - OH/HO₂: Stratospheric/mesospheric profiles only (Aura/MLS)
 - RO/RO₂: No data

Sporadic measurements

- Some aircraft/balloons (at 30–40 km) campaigns (OH and $\sum(\text{RO}_2 + \text{HO}_2)$)
- Short-term field studies (no reference data for long-term trends)

Challenges: Short lifetimes (<1 s to minutes), low concentrations (ppq–ppt level), instrument interference, and no calibration standards.

Organic Peroxy Radicals (ROO•) in Atmospheric Chemistry

Introducing volatile organic compounds into atmospheric chemistry

In the presence of 20% atmospheric O₂, alkyl radicals react within **nanoseconds**:

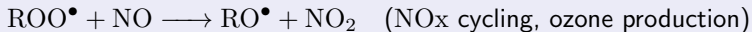


- ROO• = Organic peroxy radical (is thus the key intermediate of the VOCs chemistry)
- Critical question: **What controls ROO• reactivity?**

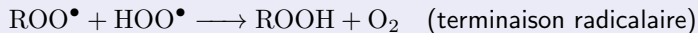
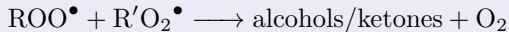
Organic Peroxy Radicals ($\text{ROO}^\bullet$) in Atmospheric Chemistry

What is admitted: $\text{ROO}^\bullet$ Reaction Pathways

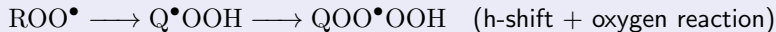
- **With NO** (polluted air):



- **With $\text{HOO}^\bullet$ or other $\text{ROO}^\bullet$** (clean/pristine air):



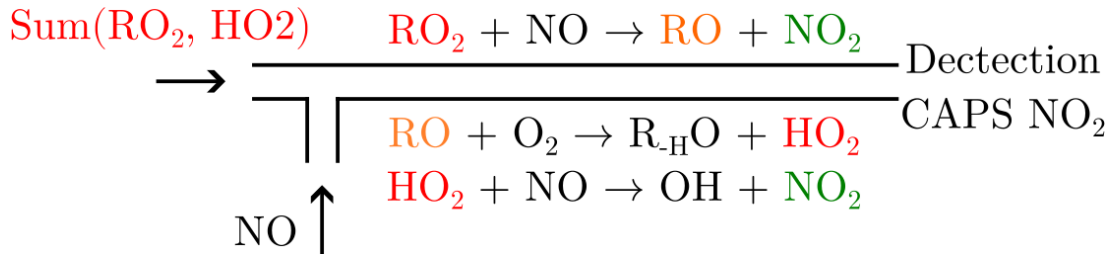
- **Or autoxidation**, toward formation of HOMs (highly oxygenated molecules):



PERCA technique (Peroxy Radical Chemical Amplification)

The only RO_x measurement method used in the field relies on NO titration.

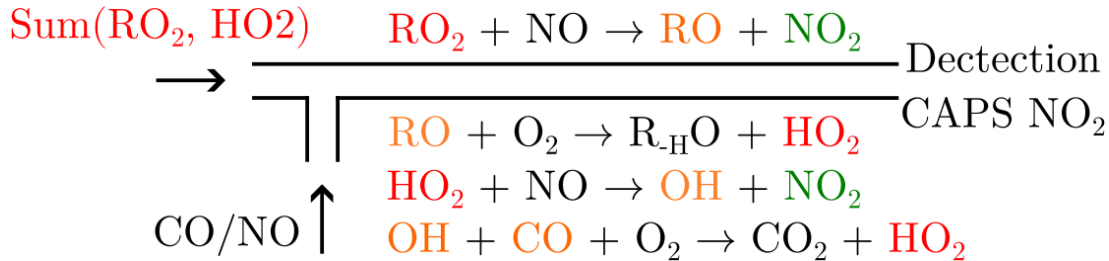
Principle:



PERCA technique (Peroxy Radical Chemical Amplification)

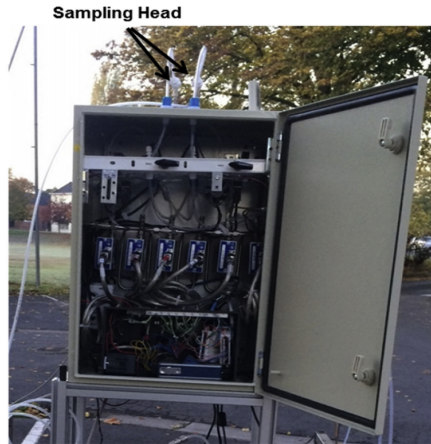
The only ROx measurement method used in the field relies on NO titration.

Principle:



PERCA Technique (Peroxy Radical Chemical Amplification)

- Complex calibration.
- Chain-length sensitive to the relative humidity (10–30 amplification factors).
- Frequent intercomparison campaigns in atmospheric simulation chambers.
- Only half a dozen laboratories worldwide have the expertise.



Credit: Clara Strunz

Mass spectrometry: that's easy!

Ions are detected!

How?

(i) producing ions

- electron removal: electron gun, electron spray, laser, synchrotron radiation, radioactive source....
- chemical ionization: electron transfer, proton transfer (H_3O^+ , NH_4^+) or any chemical (I^+ , SO_3^- , Ar^+ , ...)

(ii) detecting ions

- Hemispheric analyzer
- Quadrupole
- Time-of-flight
- Orbitrap
- ...

Mass spectrometry: that's easy!

Ions are detected!

How?

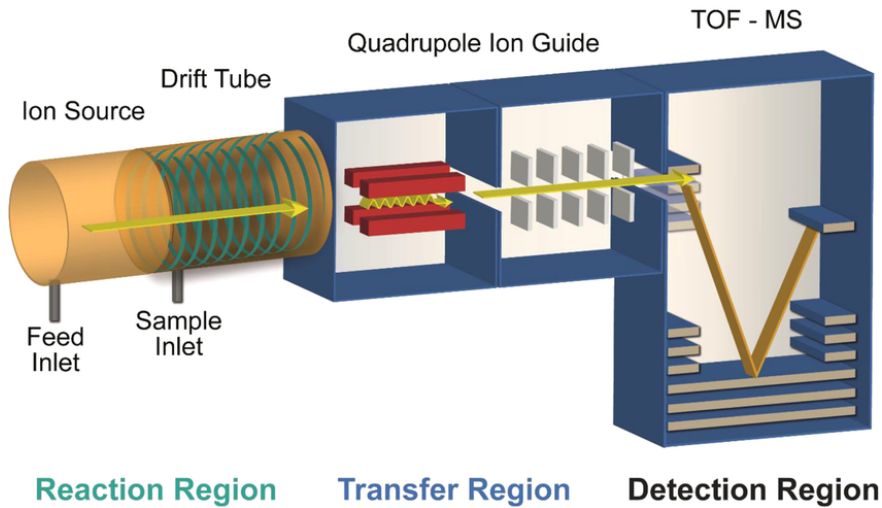
(i) producing ions

- electron removal: electron gun, electron spray, laser, synchrotron radiation, radioactive source....
- **chemical ionization**: electron transfer, **proton transfer** (H_3O^+ , NH_4^+) or any chemical (I^+ , SO_3^+ , Ar^+ , ...)

(ii) detecting ions

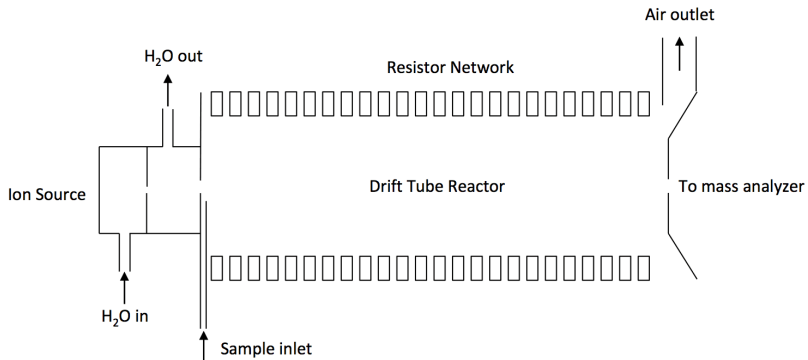
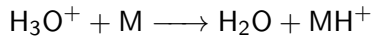
- Hemispheric analyzer
- Quadrupole
- **Time-of-flight**
- Orbitrap
- ...

Proton-Transfer-Reaction Mass Spectrometry

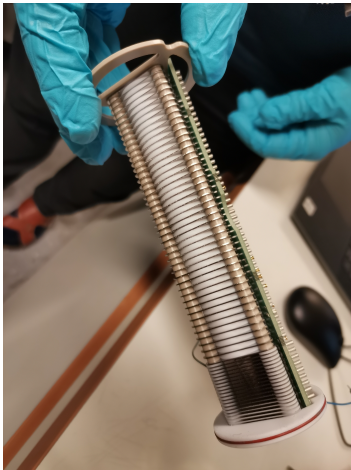
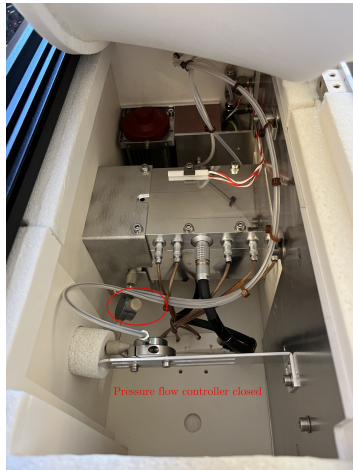


Hegen et al. 2022

Ionisation schematic



Drift tube

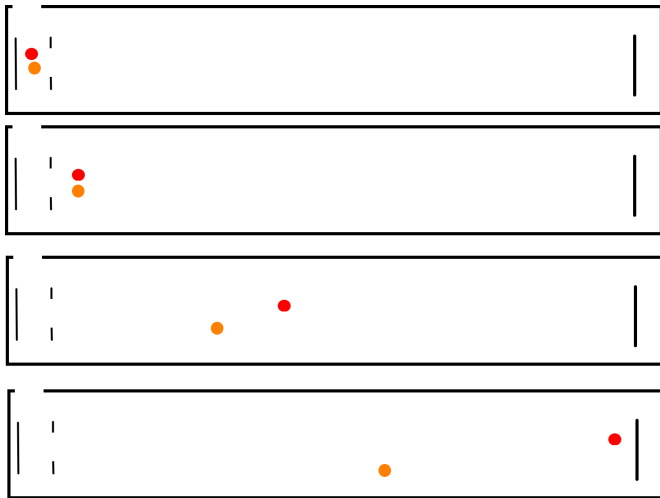


Chemical ionisation

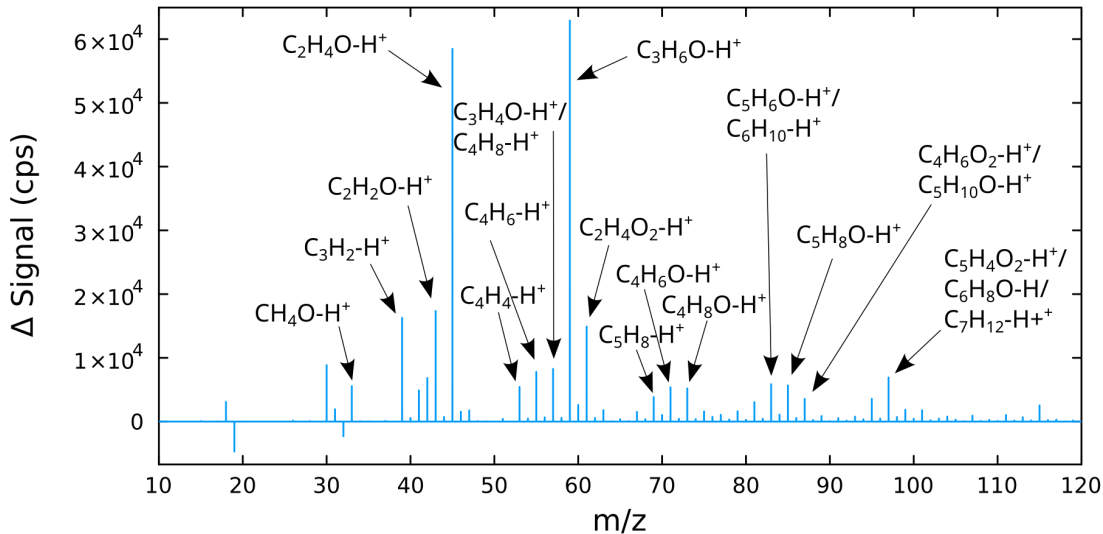
Water wapor discharge $\rightarrow \text{H}_3\text{O}^+$



Time-of-flight: principle - energy conservation, velocity separation

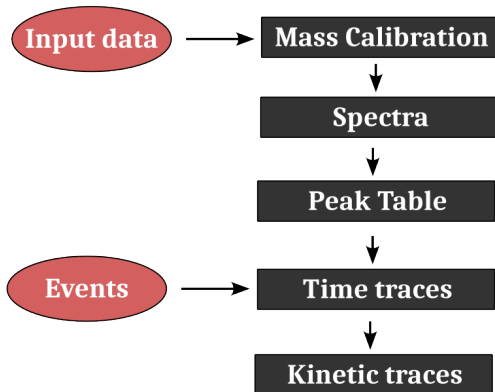


A typical mass spectrum



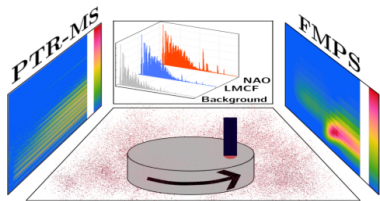
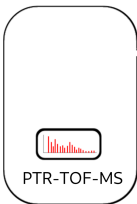
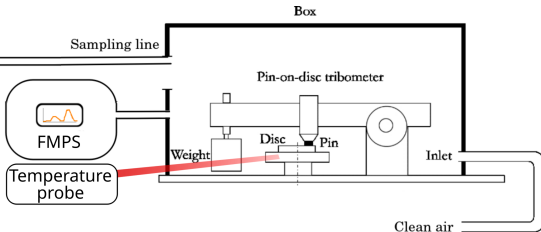
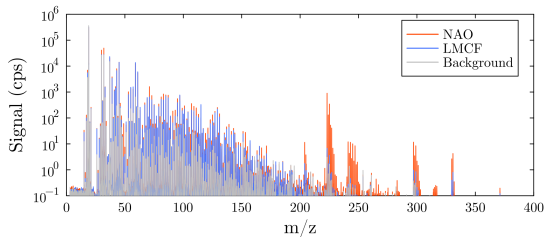
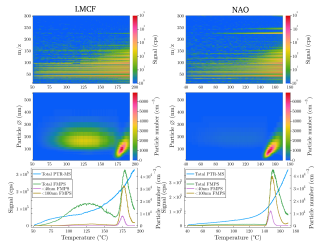


MassSpec.jl



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

Application to Air quality Measurements: Detecting VOCs



Coupling PTR-TOF-MS with an Atmospheric Reactor

PTR-TOF-MS Capabilities

- **Broad VOC detection:** Real-time monitoring of >200s of VOCs (ppt–ppb).
- **High resolution:** $m/\Delta m \sim 7000$.
- **Processing data tools:** MassSpec package within Julia's ecosystem.

Atmospheric Reactor System

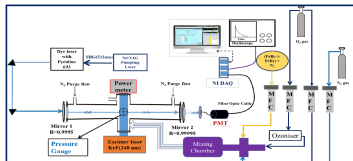
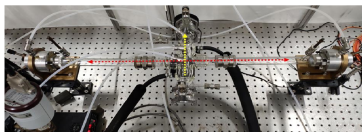
- **Purpose:** Study chemistry in a controlled environment.
- **Controlled over:** the chemistry, RH/Temperature and reaction time.

Which laboratory method for an atmospheric reactor?

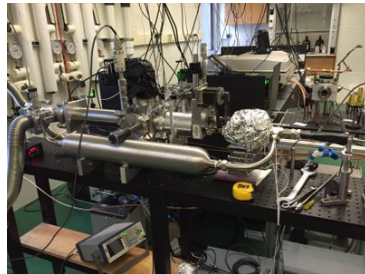
Laboratory studies



Atmospheric simulation chamber. Illustration Eurochamp website, EUPHORE (Spain)

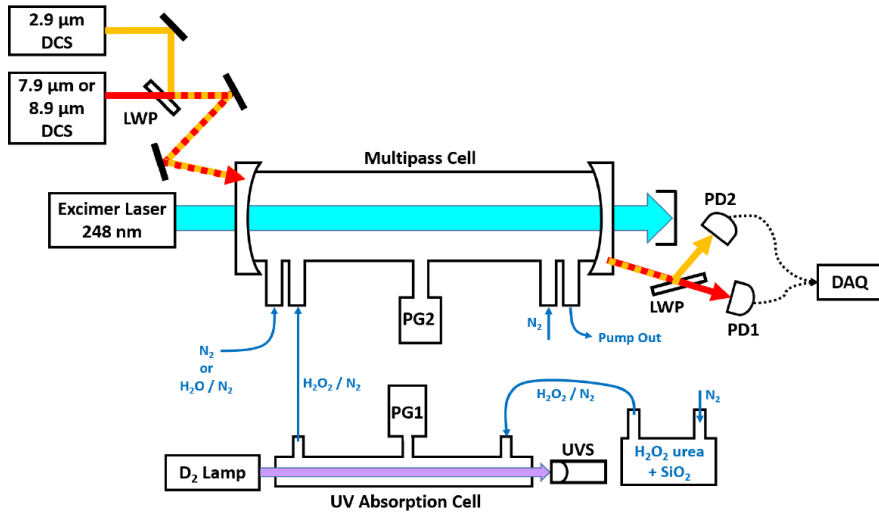


Photolysis cell. Illustration Rajakumar's lab website (India)



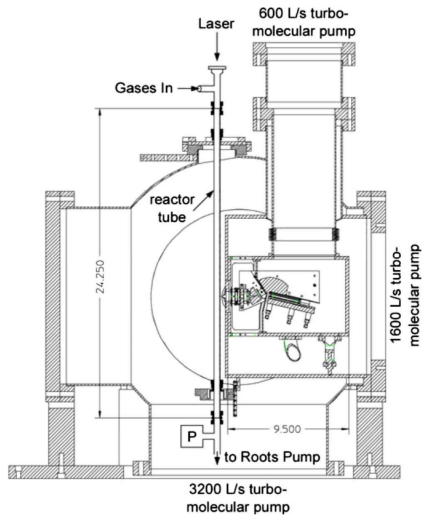
Fast flow reactor. Illustration Goulay's lab website (USA).

Kinetics Experiment by Optical Spectroscopy



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

Kinetics Experiment by Mass Spectrometry



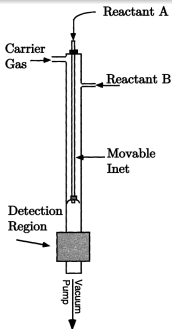
Osborn et al., 2008 (RSI)

Classical Flow Tube Reactor

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

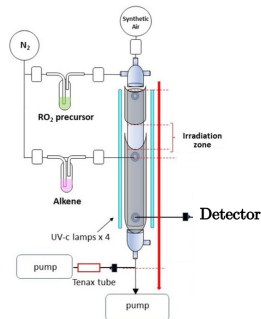
Injector

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

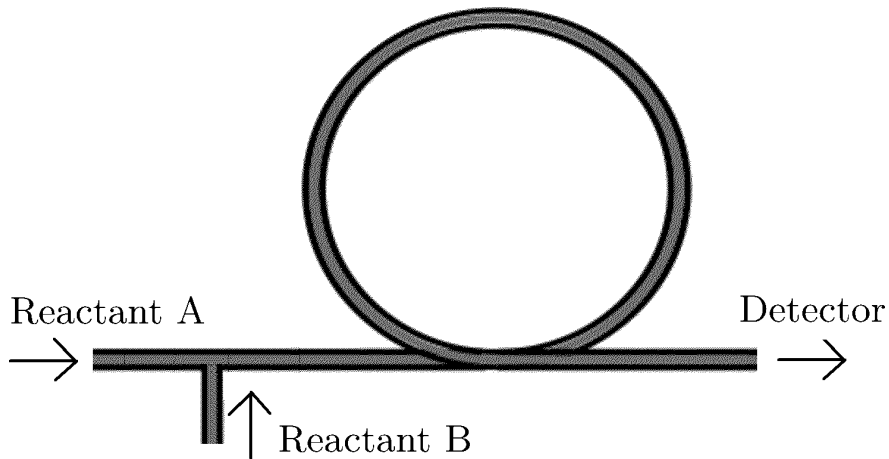


Movable photolysis window

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

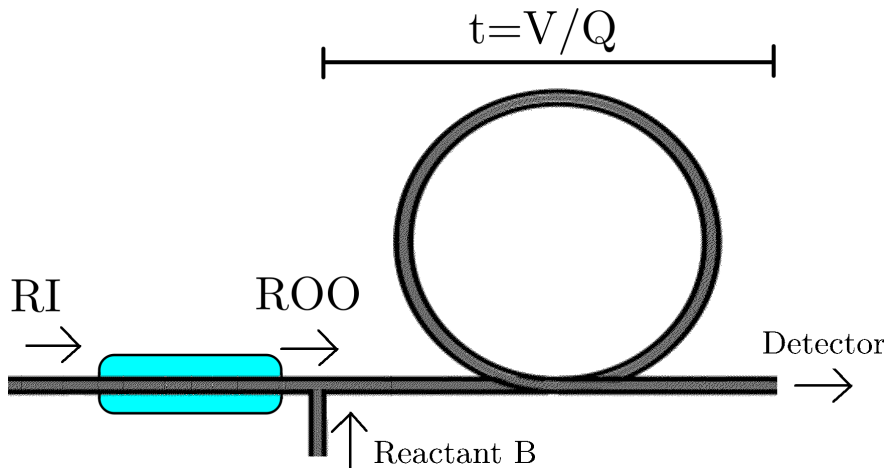


A Simple Flow Tube for Chemical Kinetics



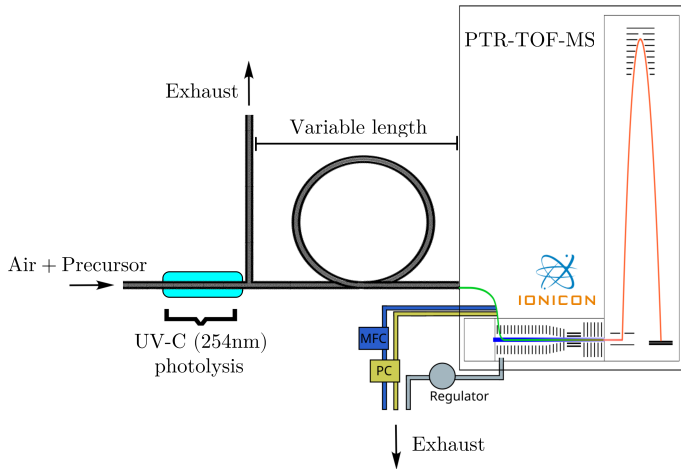
Simply what we need for chemical kinetics.

A Simple Flow Tube for Chemical Kinetics



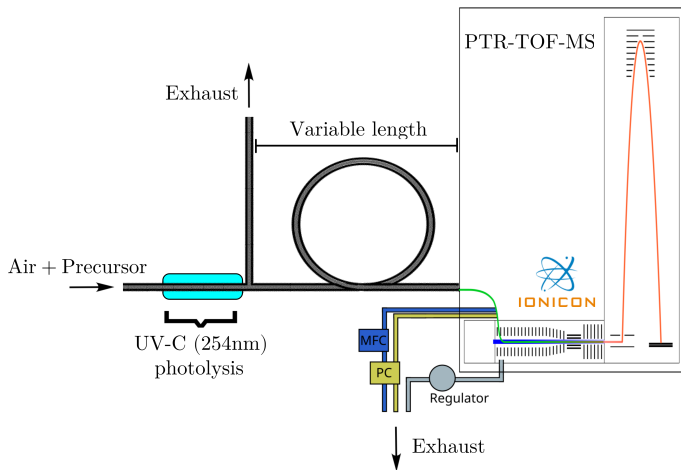
Simply what we need for chemical kinetics of organic peroxy radicals.

The Coupling with a PTR-TOF-MS



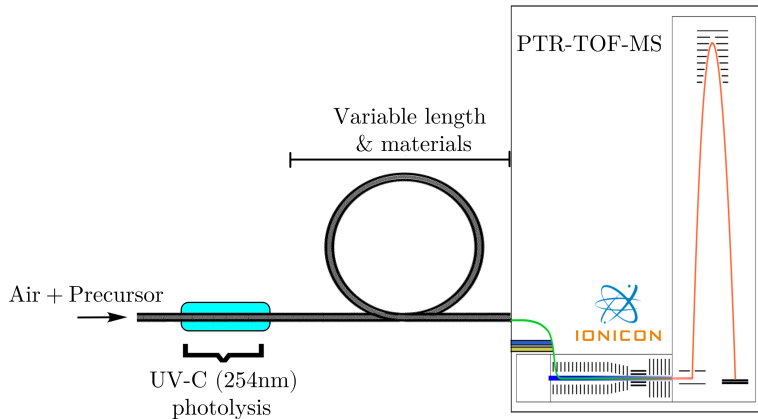
Flow Tube Reactor

Which material to use for the flow tube reactor to study RO_2 ?

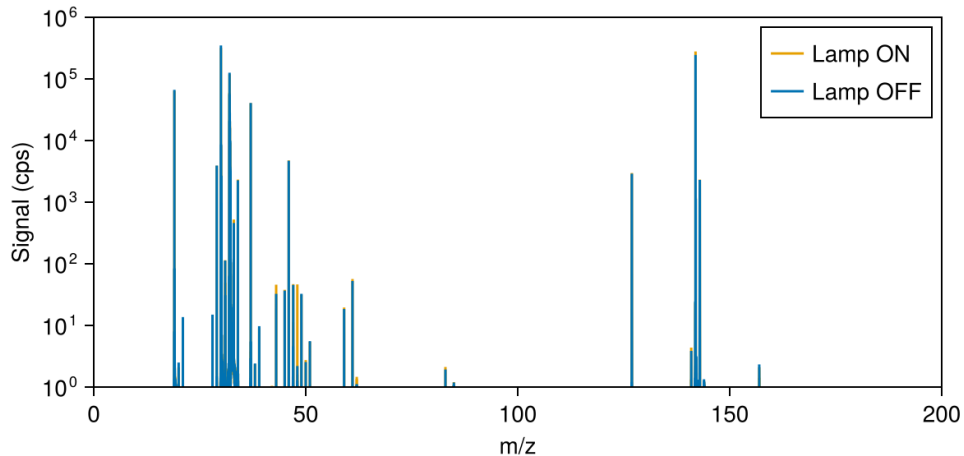


Uptake on Walls

- PFA
- Glass
- Copper
- Brass
- Stainless Steel
- Aluminum

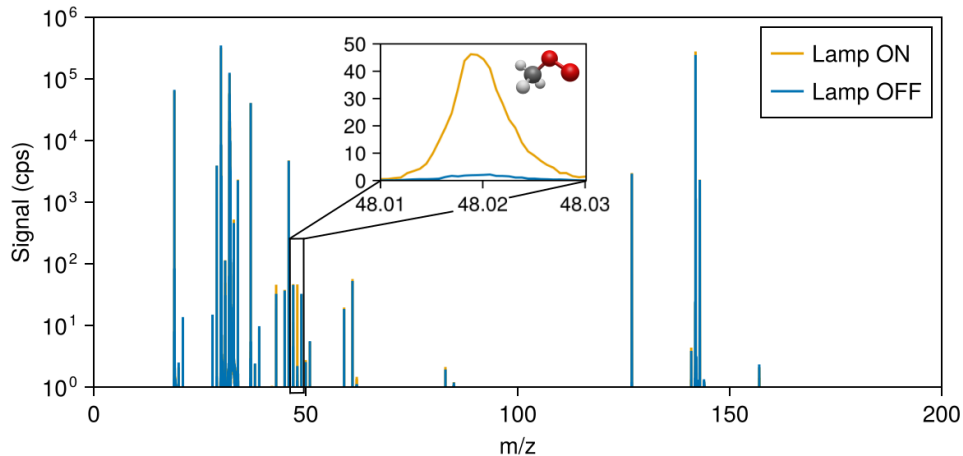


Uptake on Walls



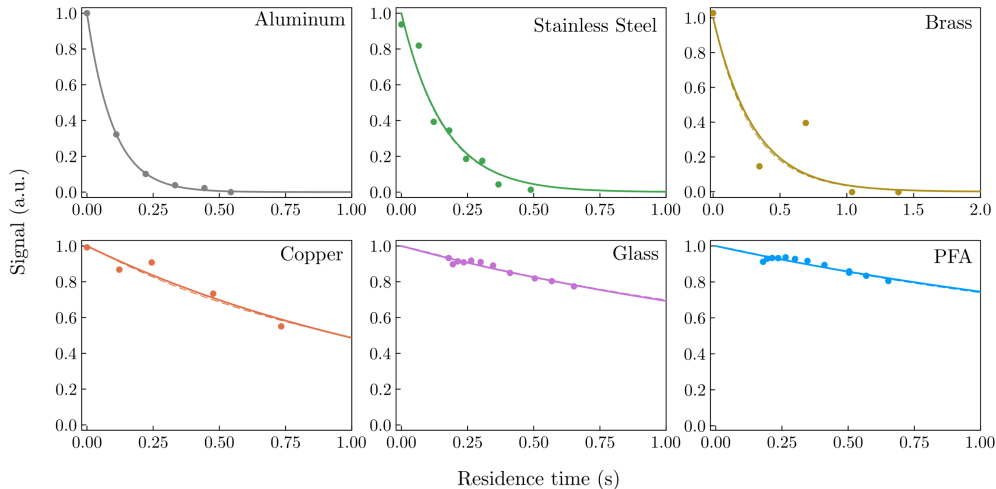
Typical mass spectrum recorded for one kinetic point.

Uptake on Walls



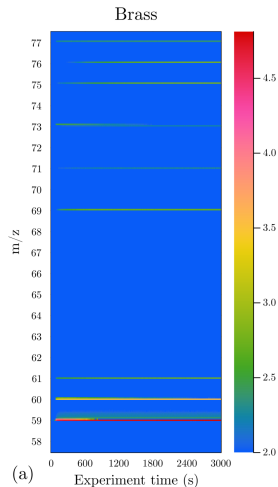
Direct detection of $\text{CH}_3\text{OO}\cdot$ at ppb sensitivity.

Uptake on Walls



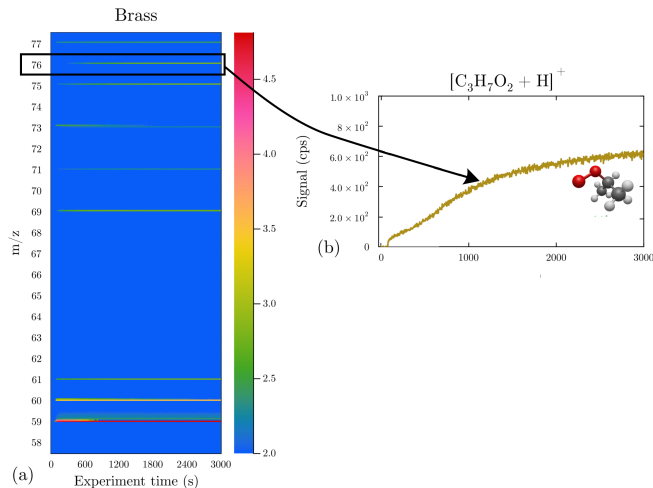
Kinetics measurements using different reactor materials.

Uptake on Walls



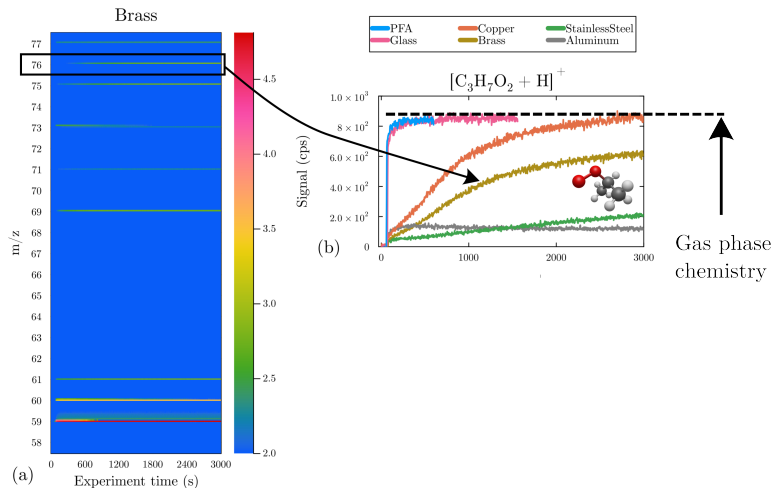
Durif et al, 2024 (JACS Au), DOI:10.1021/jacsau.4c00060
Dataset, DOI: 10.5281/zenodo.10790197

Uptake on Walls



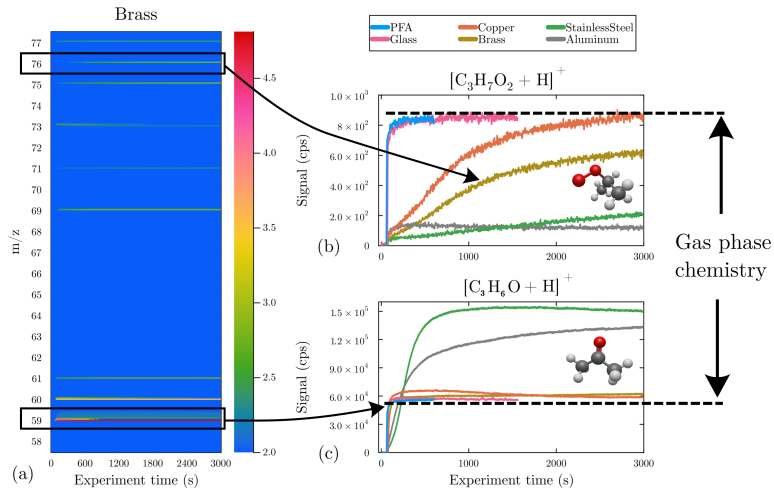
Durif et al, 2024 (JACS Au), DOI:10.1021/jacsau.4c00060
Dataset, DOI: 10.5281/zenodo.10790197

Uptake on Walls



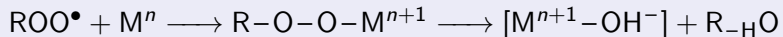
Durif et al, 2024 (JACS Au), DOI:10.1021/jacsau.4c00060
Dataset, DOI: 10.5281/zenodo.10790197

Uptake on Walls



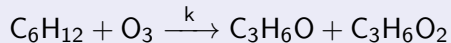
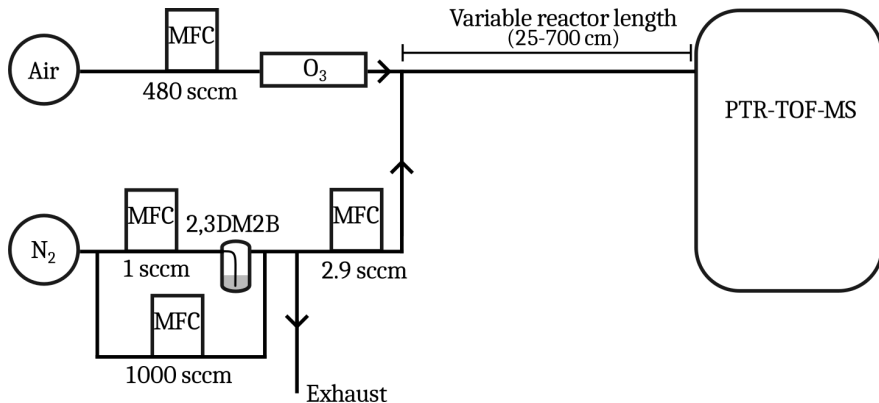
Durif et al, 2024 (JACS Au), DOI:10.1021/jacsau.4c00060
Dataset, DOI: 10.5281/zenodo.10790197

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

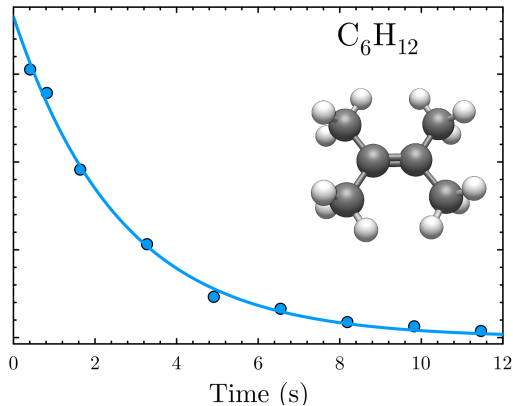
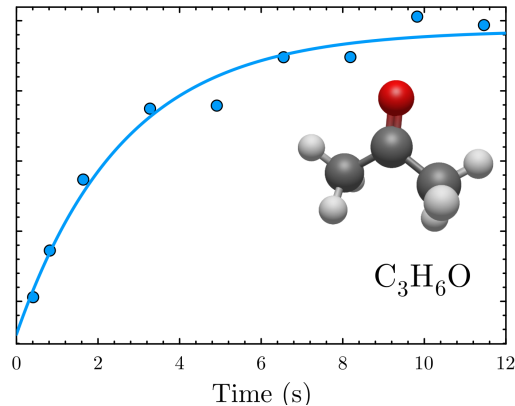


Validation of the approach: test system

2,3-dimethyl-2-butene Ozonolysis



Test system: 2,3-dimethyl-2-butene Ozonolysis



Result: $k = 2.1 \times 10^{-15} \text{ cm}^3/\text{molecules}^{-1} \text{ s}^{-1}$.

IUPAC recommendation: $k = 1.1 \times 10^{-15} \text{ cm}^3/\text{molecules}^{-1} \text{ s}^{-1}$.

IUPAC values: 2,3-dimethyl-2-butene Ozonolysis



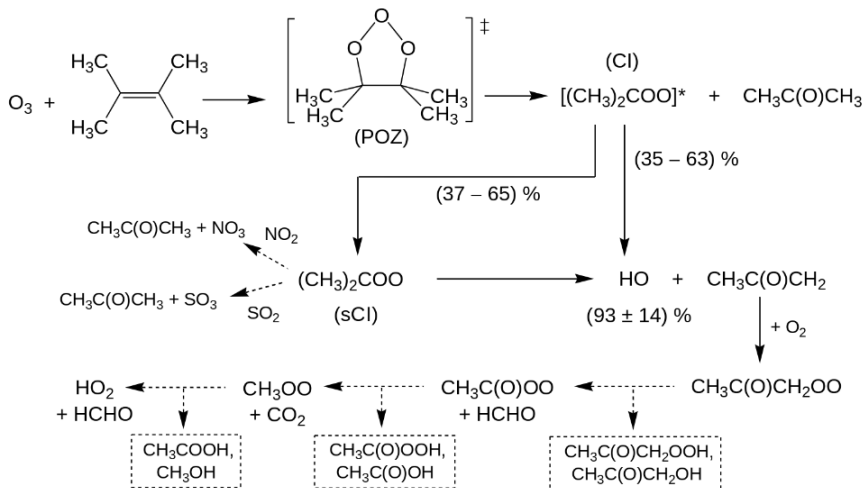
Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.51 \pm 0.08) \times 10^{-15}$	299 ± 2	Japar et al., 1974	S-CL/GC-FID (a)
$2.82 \times 10^{-15} \exp[-(294 \pm 196)/T]$	227-363	Huie and Herron, 1975	MS/MS (a)
1.05×10^{-15}	298*		
$(1.0 \pm 0.2) \times 10^{-15}$	295 ± 0.5	Witter et al., 2002	S-UVA/FTIR (b)
<i>Relative Rate Coefficients</i>			
$(1.24 \pm 0.11) \times 10^{-16}$	296 ± 2	Greene and Atkinson, 1992	RR/GC-FID (c)

Previous studies: excess DMB. Here, excess Ozone.

Hypothesis: 2 DMB for 1 ozone due to secondary reactions?

IUPAC Mechanism: 2,3-dimethyl-2-butene Ozonolysis

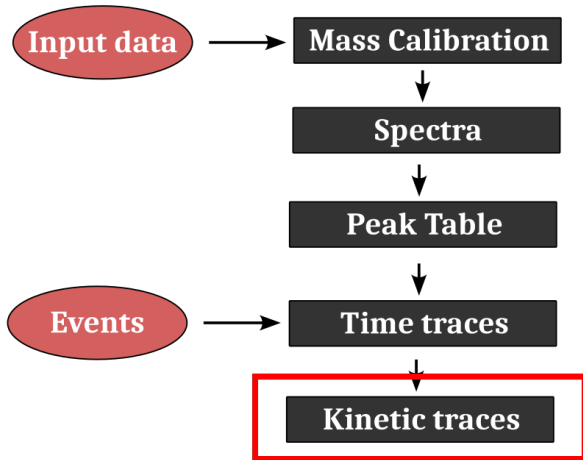


Are these products or any other in our data?

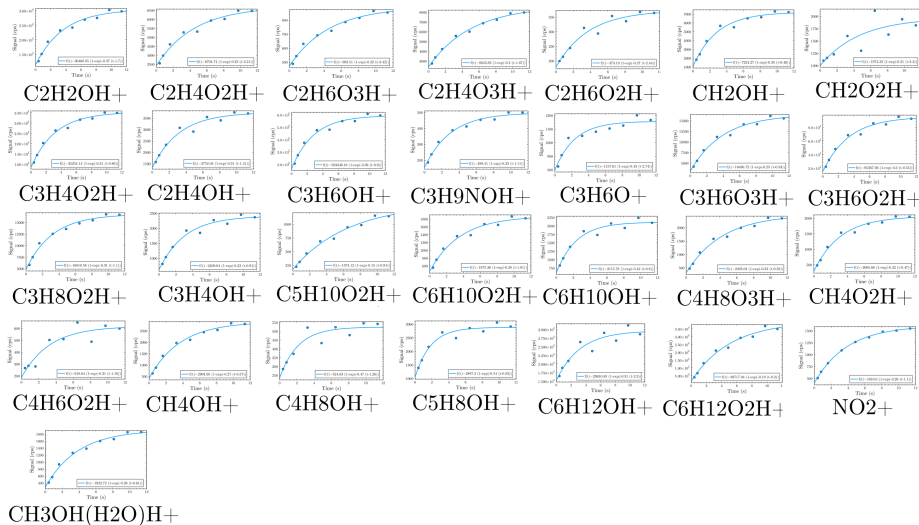
Data processing: 2,3-dimethyl-2-butene Ozonolysis

julia

MassSpec.jl



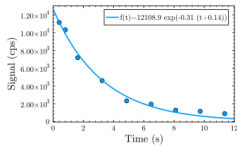
Products: 2,3-dimethyl-2-butene Ozonolysis



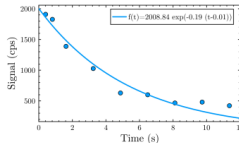
29 products identified by their kinetic trace.

Reactants: 2,3-dimethyl-2-butene Ozonolysis

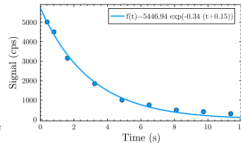
But also 5 reactants involves.



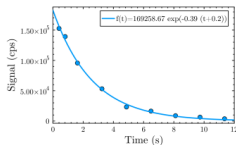
C3H6H+



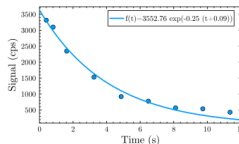
C3H4H+



C5H8H+



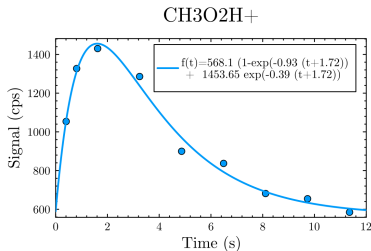
C6H12H+



C6H11H+

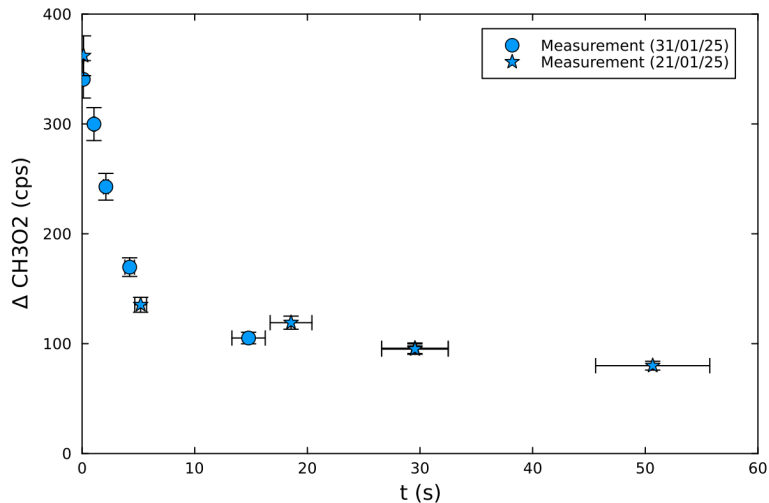
Intermediate: 2,3-dimethyl-2-butene Ozonolysis

And 1 intermediate observed... guess who.



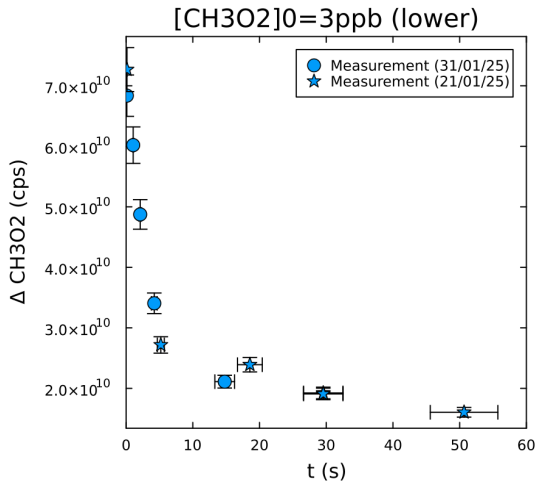
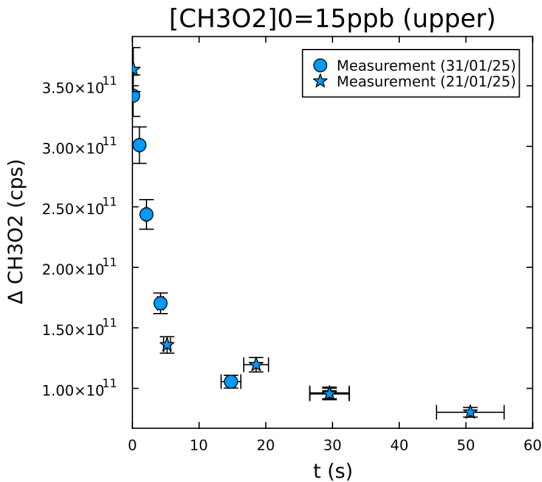
Complex chemical system, I'm pretty happy with $k = 2.1 \times 10^{-15} \text{ cm}^3/\text{molecules}^{-1} \text{ s}^{-1}$.

The CH_3O_2 mystery

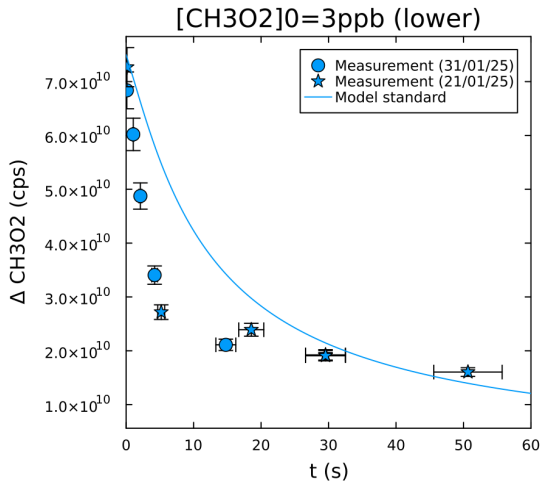
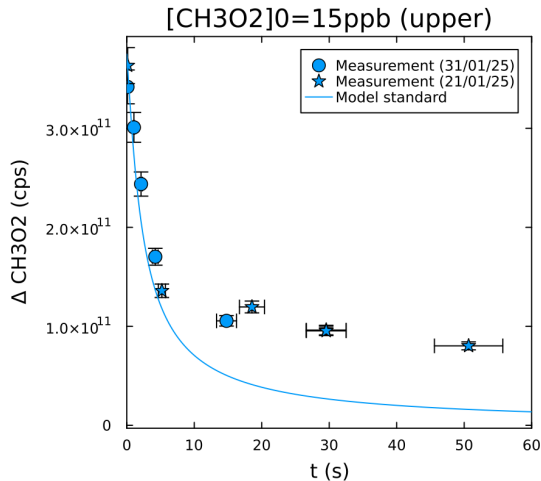


- $[\text{CH}_3\text{I}] = 2.1$ ppm.
- Titration: $[\text{NO}_2] = 30$ ppb with large NO excess $\Rightarrow$ assuming 15 ppb of $[\text{CH}_3\text{O}_2]_0$ (probably upper case).

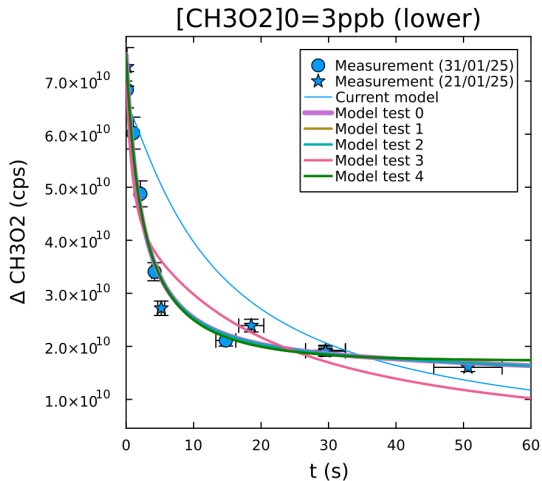
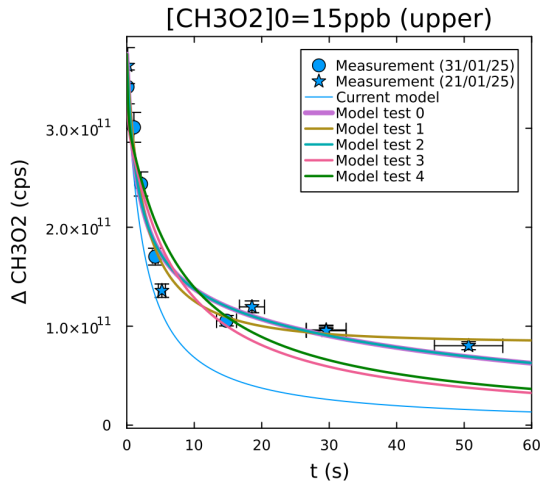
The CH_3O_2 mystery



The CH_3O_2 mystery

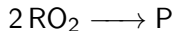


The CH_3O_2 mystery



Fitting a system

Considering only the self reaction

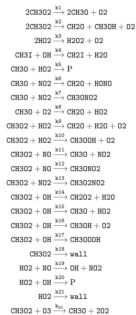


$$\frac{d[\text{RO}_2]}{dt} = -2 k [\text{RO}_2]^2$$

Analytical solution:

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

Considering a whole chemical system

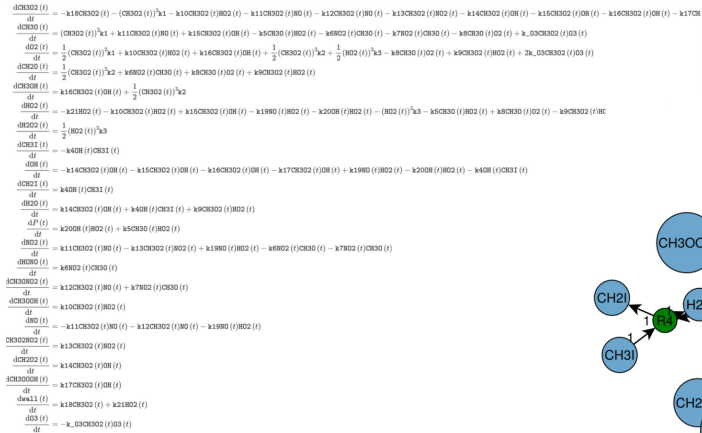
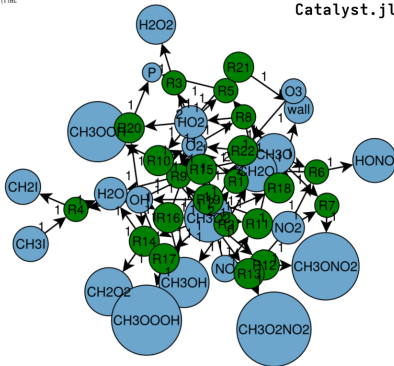


Catalyst.jl: a modern solver

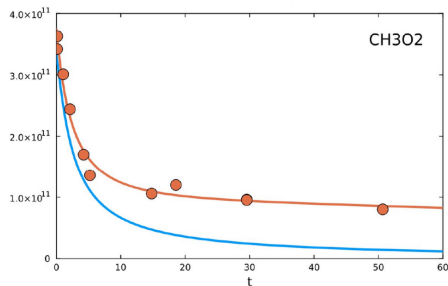
How to fit these data with a "model"?



Catalyst.jl



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	

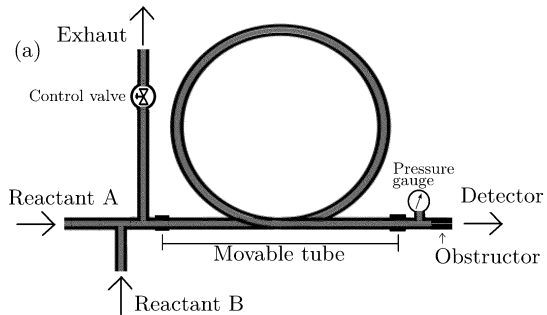
Results indicates the CH₃O₂ self reaction rate constant is, at least, one order of magnitude slower than the value reported in the IUPAC.

Last question

Can we also investigate gas-liquid and gas-surface interactions, e.g. quantify uptake by atmospherically relevant materials?

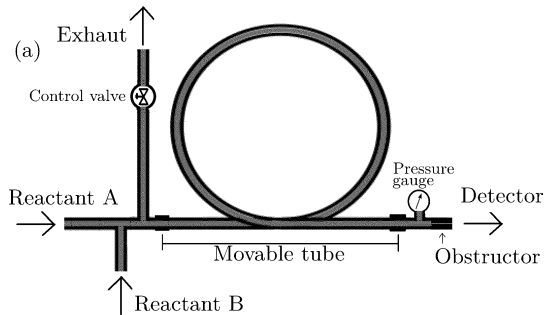
Flow Tube Variant

Varying the tube length

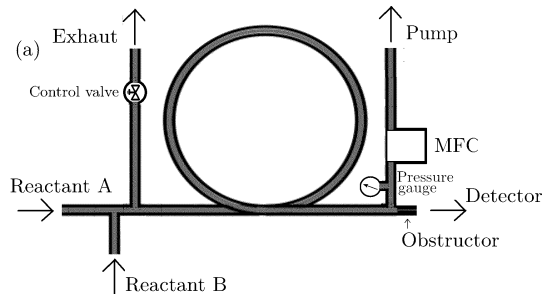


Flow Tube Variant

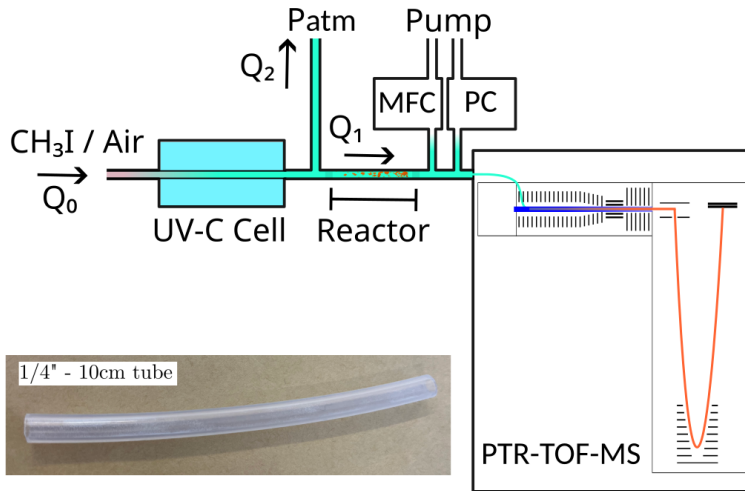
Varying the tube length



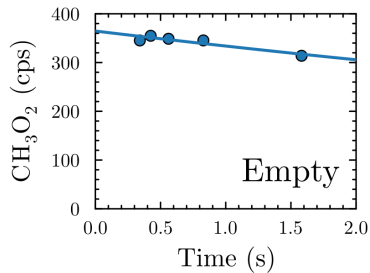
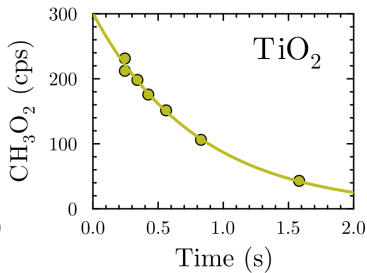
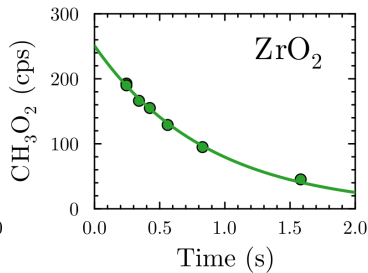
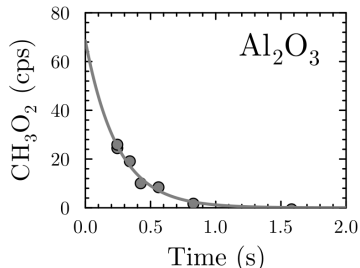
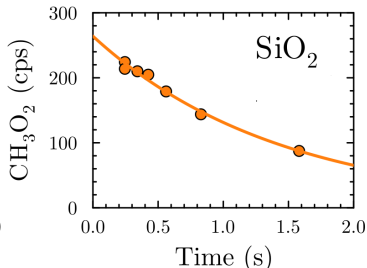
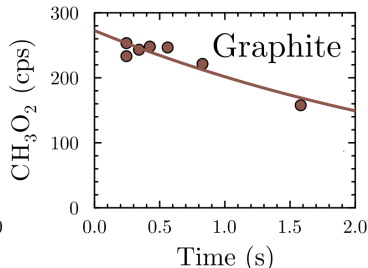
Varying the reactor flow (no mechanical parts)



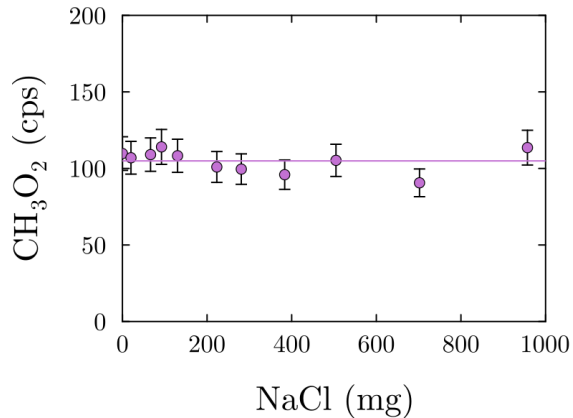
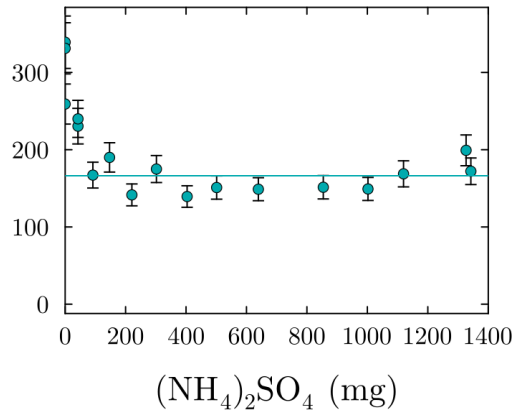
Versatile Setup for Measuring Uptake on Surfaces



Uptake on surfaces



No Uptake on Dry Salts



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 .
- When organic peroxy radicals chemistry is not dominated by reactions with NO (clean environment), then what? $\Rightarrow$ Surface reactions may matter (what about water?).
- A complete framework for PTR-MS data processing and kinetics analysis: MassSpec.jl.

EPHEMERAL Project

Pr. Barbara Nozière



The young researchers at the office

- ▶ Rafael Carvalho Couto
- ▶ Pratip Chakraborty
- ▶ Twana Cheragwandi
- ▶ Lauren Cork
- ▶ Anders Fredriksen
- ▶ Juana Salas
- ▶ Clara Strunz
- ▶ Martin van Horn

Thank you