Outline
Atmospheric Chemistry
Organic Peroxy radicals
Set-up
Results
Conclusion

GDR EMIE Plenary days

Proton-Transfer-Reaction Mass Spectrometry for Atmospheric Chemistry Applications

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Acknowledgement

Barbara Nozière

KTH VETENSKAP OCH KONST

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Outline

1. Basics of atmospheric chemistry
2. Experimental set-up
3. Surface uptake of organic peroxy radicals
4. Prospects

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Basics of atmospheric chemistry

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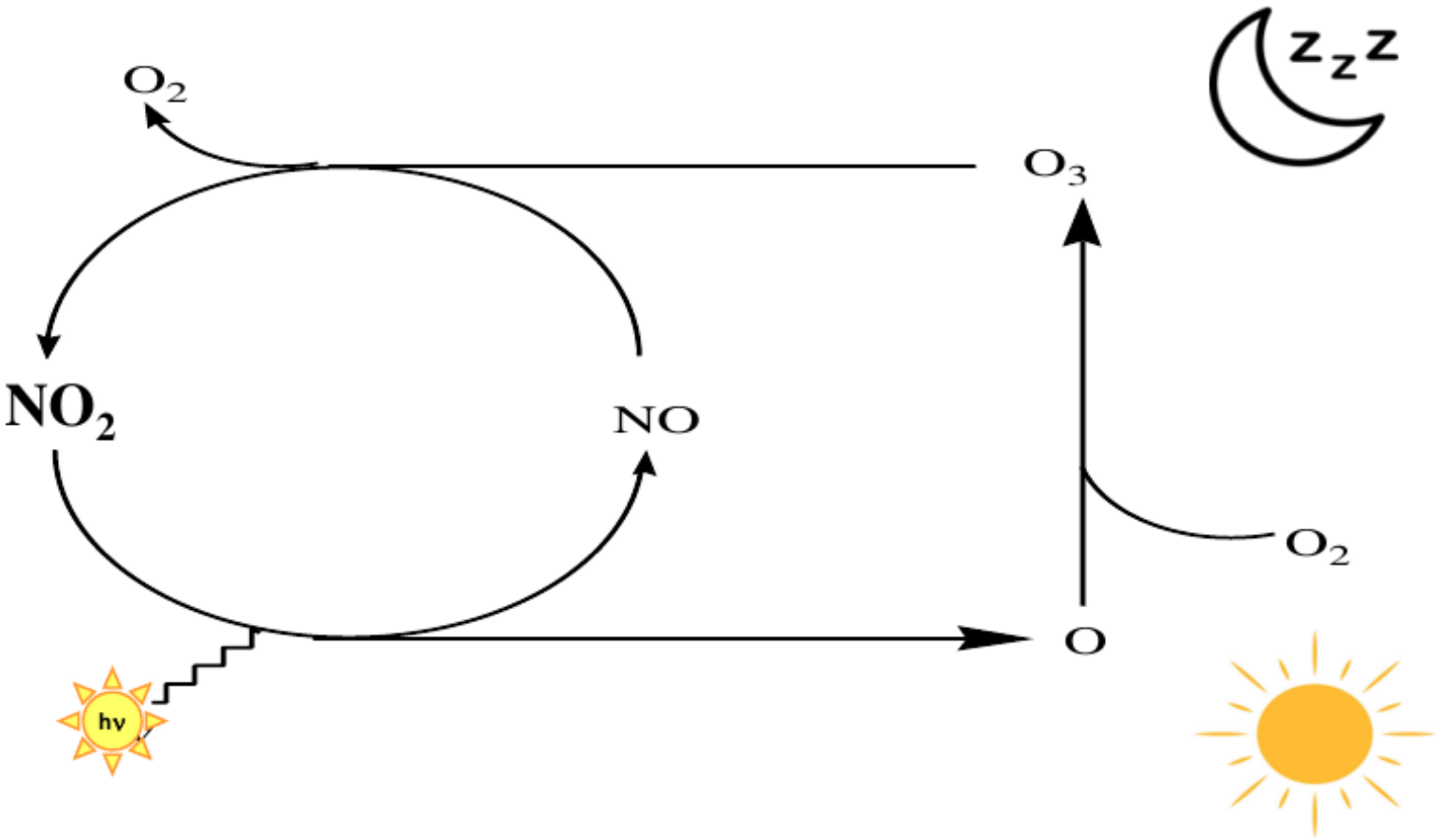

Figure: Leighton's cycle (NO/NO2/O3).

Atmospheric chemistry with VOCs !

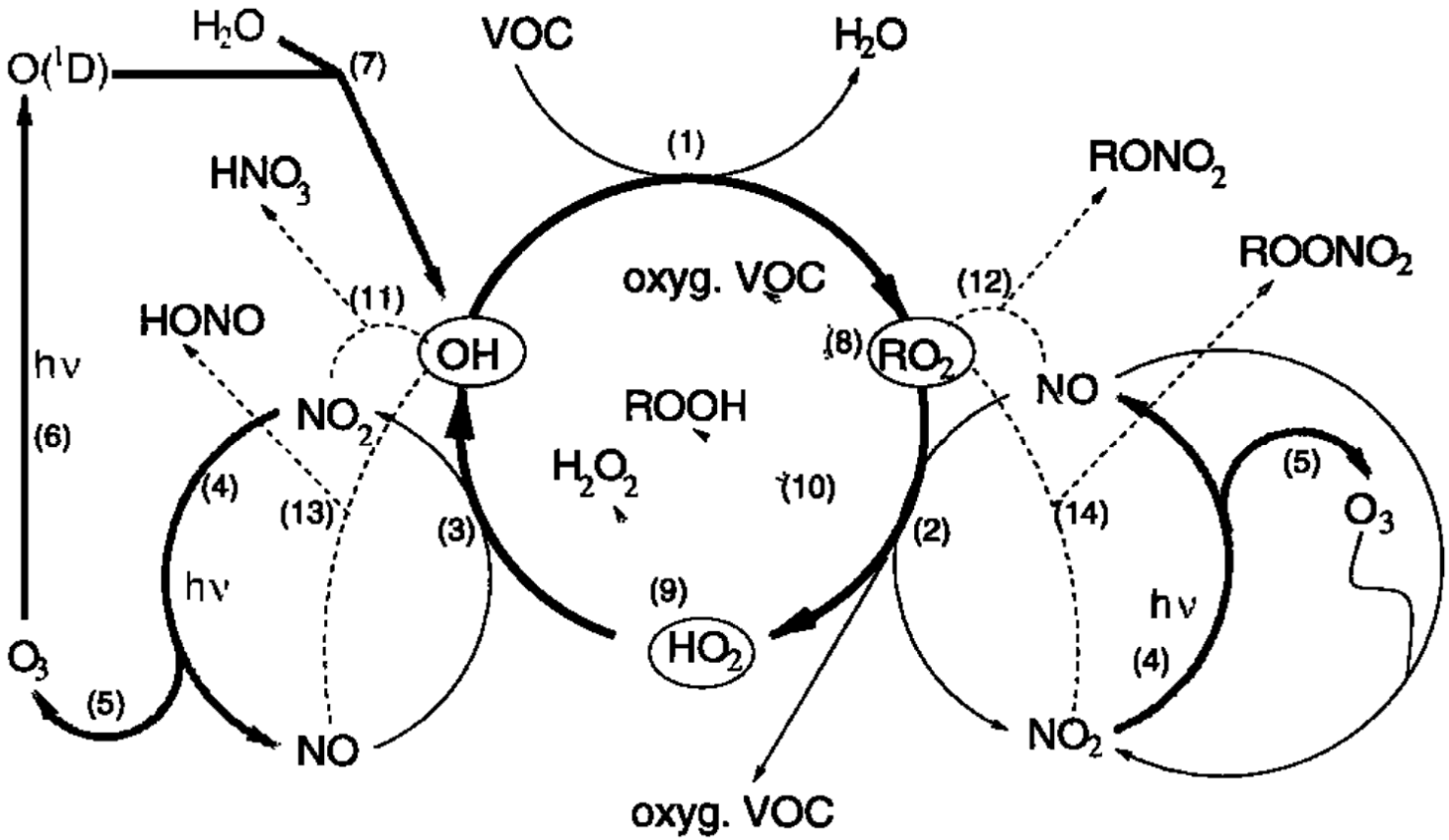

Figure: Kirchner, Frank et al., 2001, *Journal of Geophysical Research: Atmospheres*

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$ROO^{\bullet}$

- Until now, all $ROO^{\bullet}$ atmospheric measurements have been based on The Peroxy Radical Chemical Amplifier (PERCA) technique.

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- Drawback: this detection is indirect, sum all the radicals, and chemical amplification mechanisms are complex.

$ROO^{\bullet}$

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- Until now, all $ROO^{\bullet}$ atmospheric measurements have been based on The Peroxy Radical Chemical Amplifier (PERCA) technique.
- Drawback: this detection is indirect, sum all the radicals, and chemical amplification mechanisms are complex.
- Mass spectrometry provides sensitive, direct and specific measurements.

All relies on a detector

Proton-transfer-reaction mass spectrometry: a powerful method for detecting VOCs.

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Proton-transfer-reaction mass spectrometry: a powerful method for detecting VOCs.

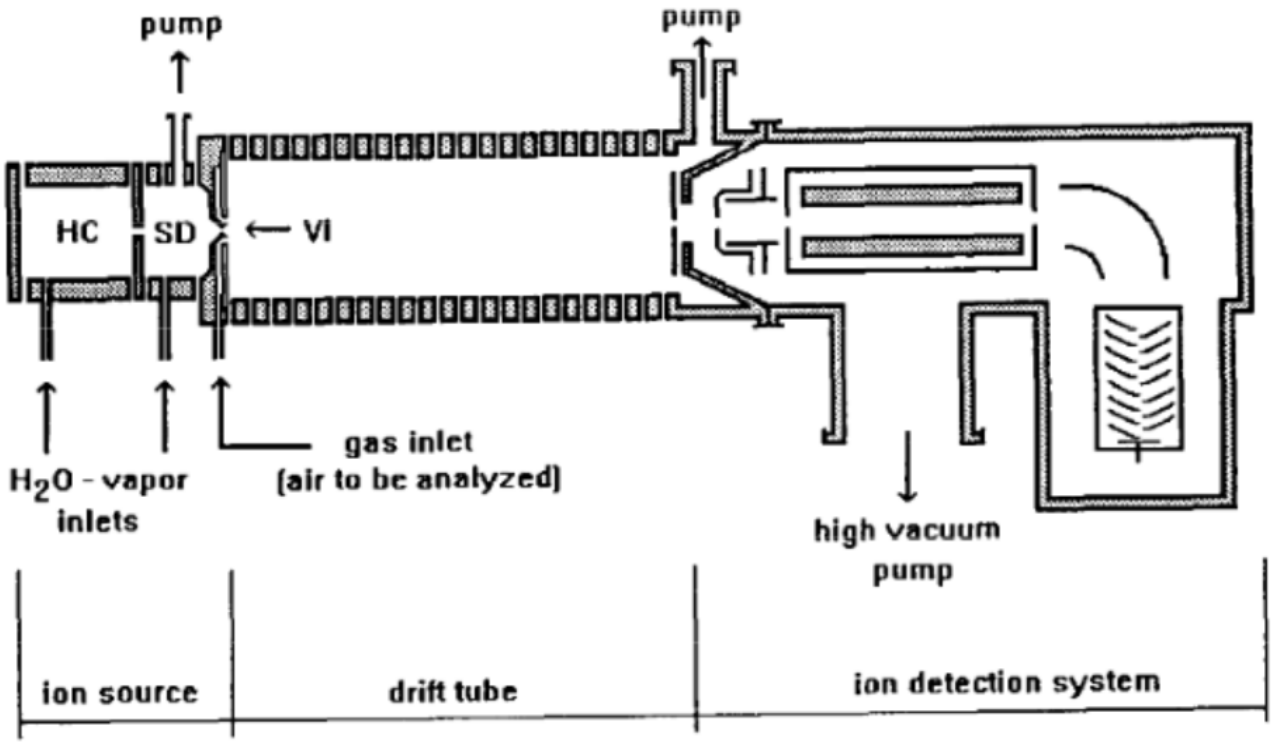

Figure: Typical PTR-MS, Warneke, C et al., 2001, *International Journal of Mass Spectrometry*

$$H_3O^+ + M \longrightarrow H_2O + MH^+$$

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But we also need a reactor

A flow tube reactor for kinetic studies of peroxy radicals.

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Classic method: cell or flow tube reactor triggered by something

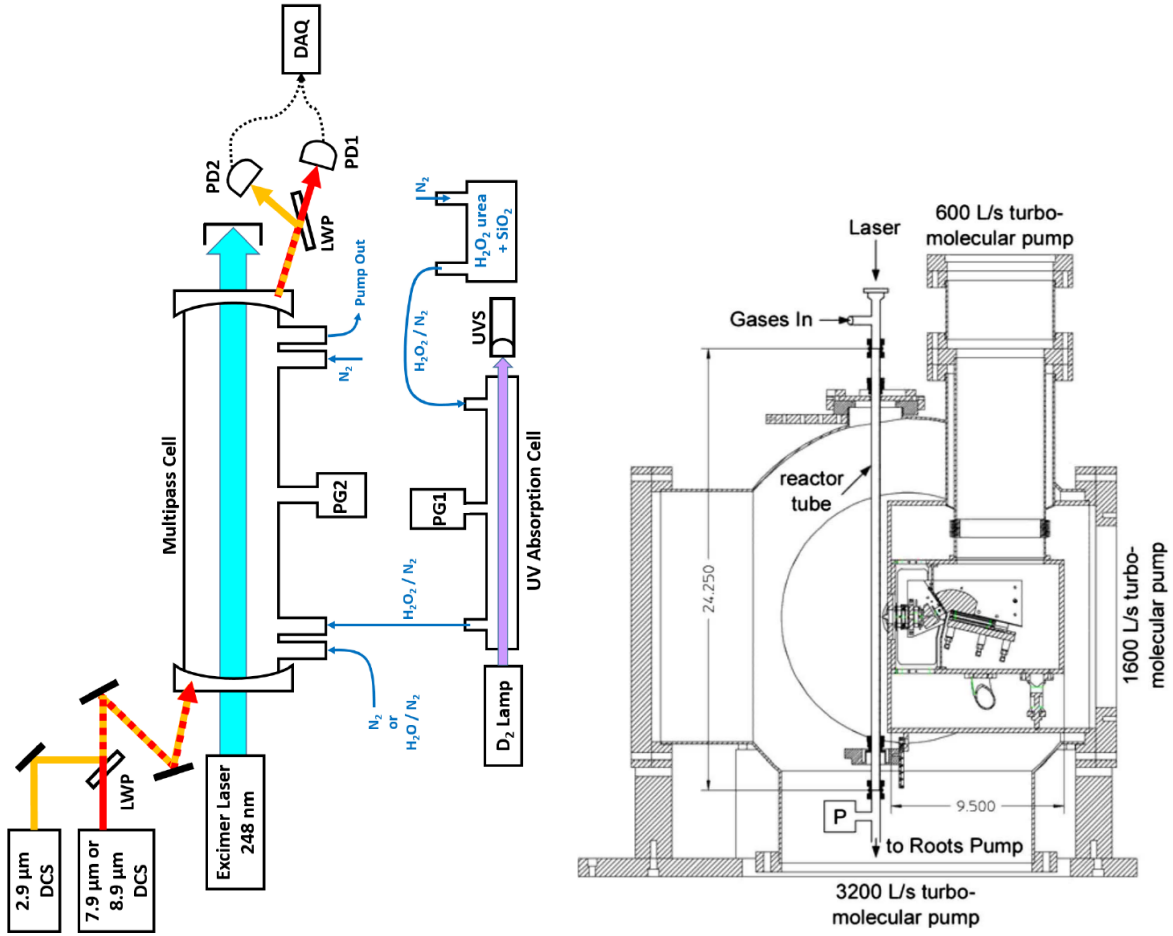

Figure: Experimental set-up by Chen, I-Yun et al., 2024, *The Journal of Physical Chemistry Letters* and Osborn, David L. et al., 2008, *Review of Scientific Instruments*

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The other classical method: continuous photolysis using a lamp and a flow injector

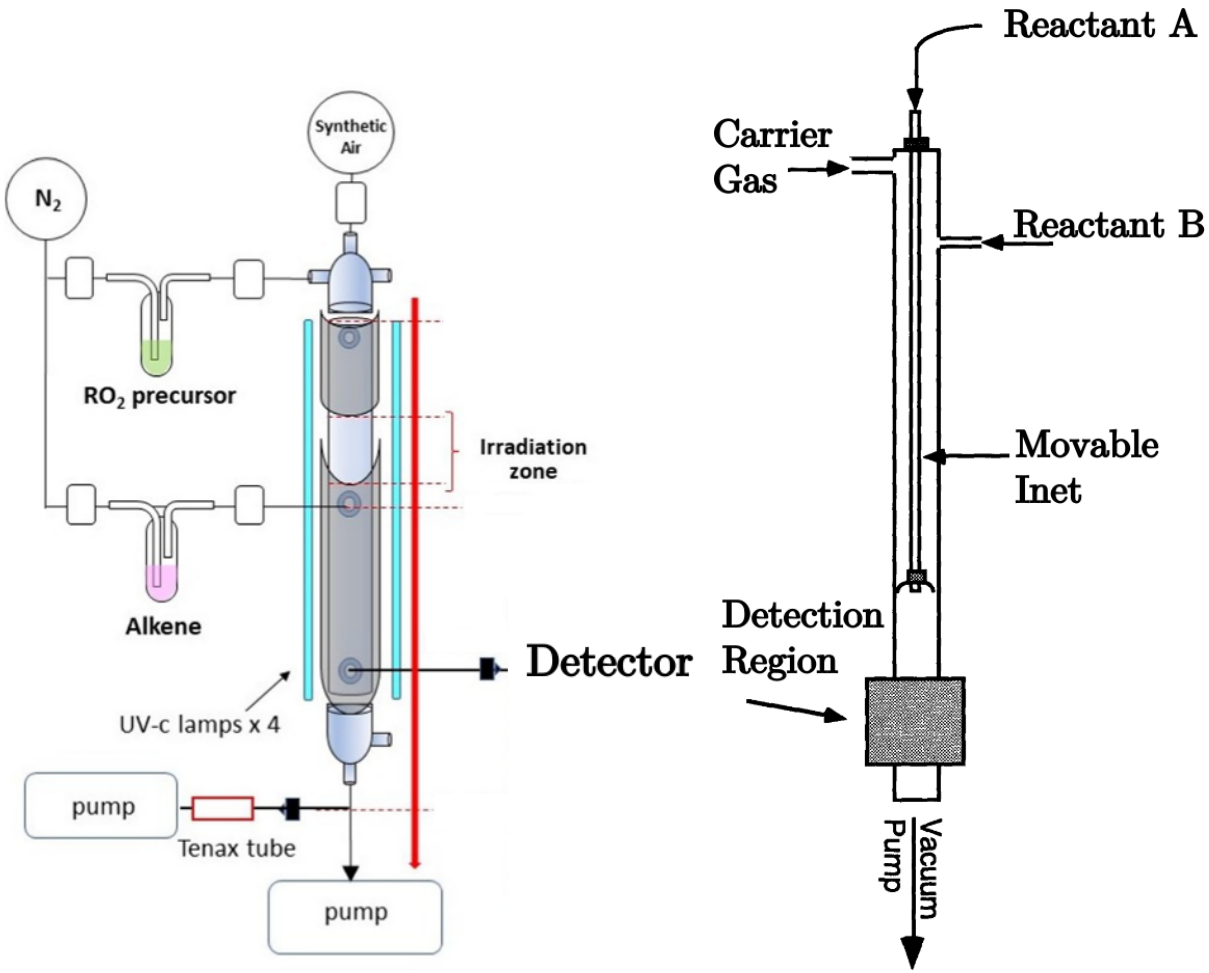

Figure: Experimental set-up Nozière, Barbara et al., 2023, *Physical Chemistry Chemical Physics* and movable injector

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Simple alternative chemical kinetics method

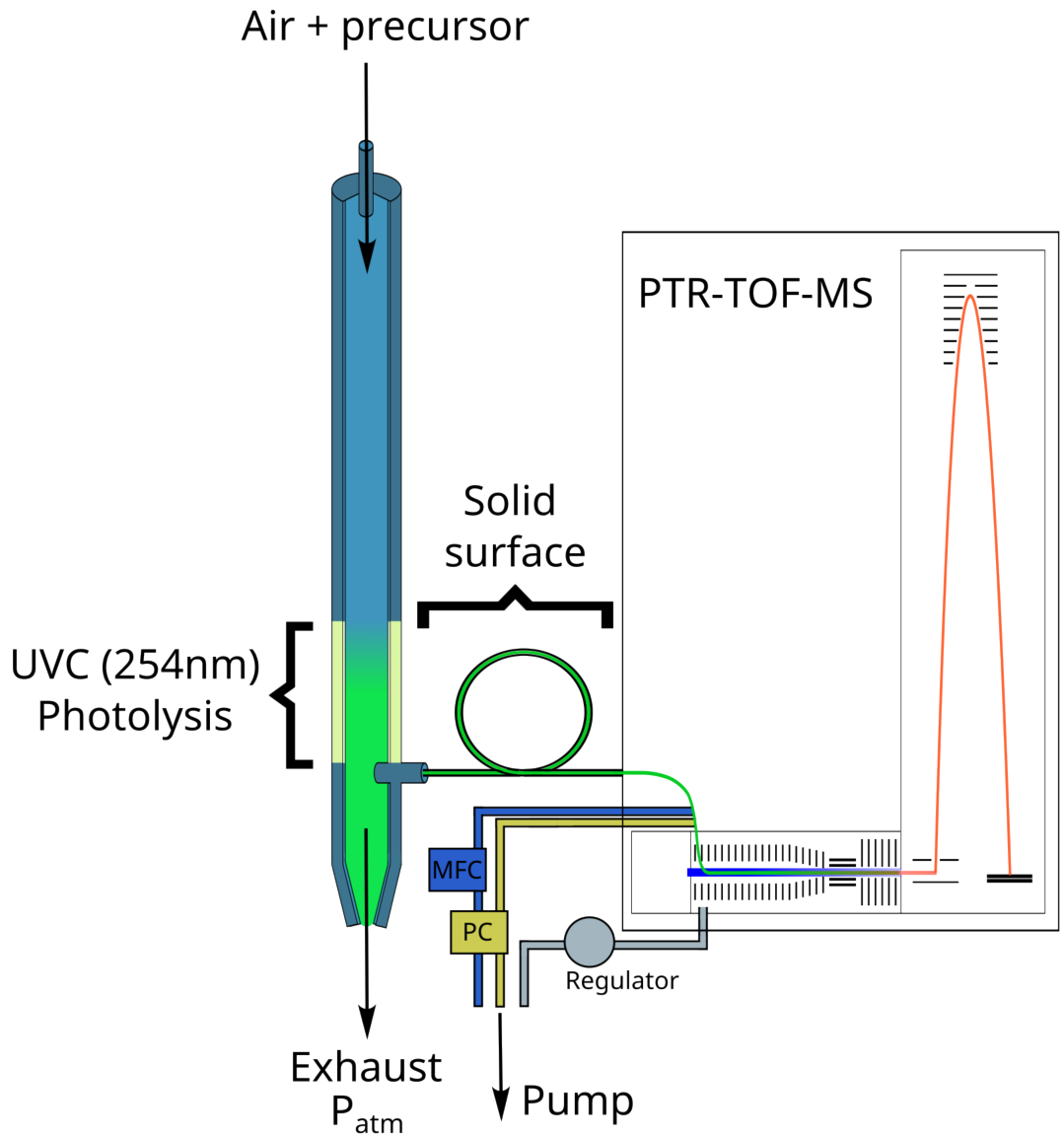

Figure: Experimental set-up by Durif, Olivier et al., 2024, *JACS Au*

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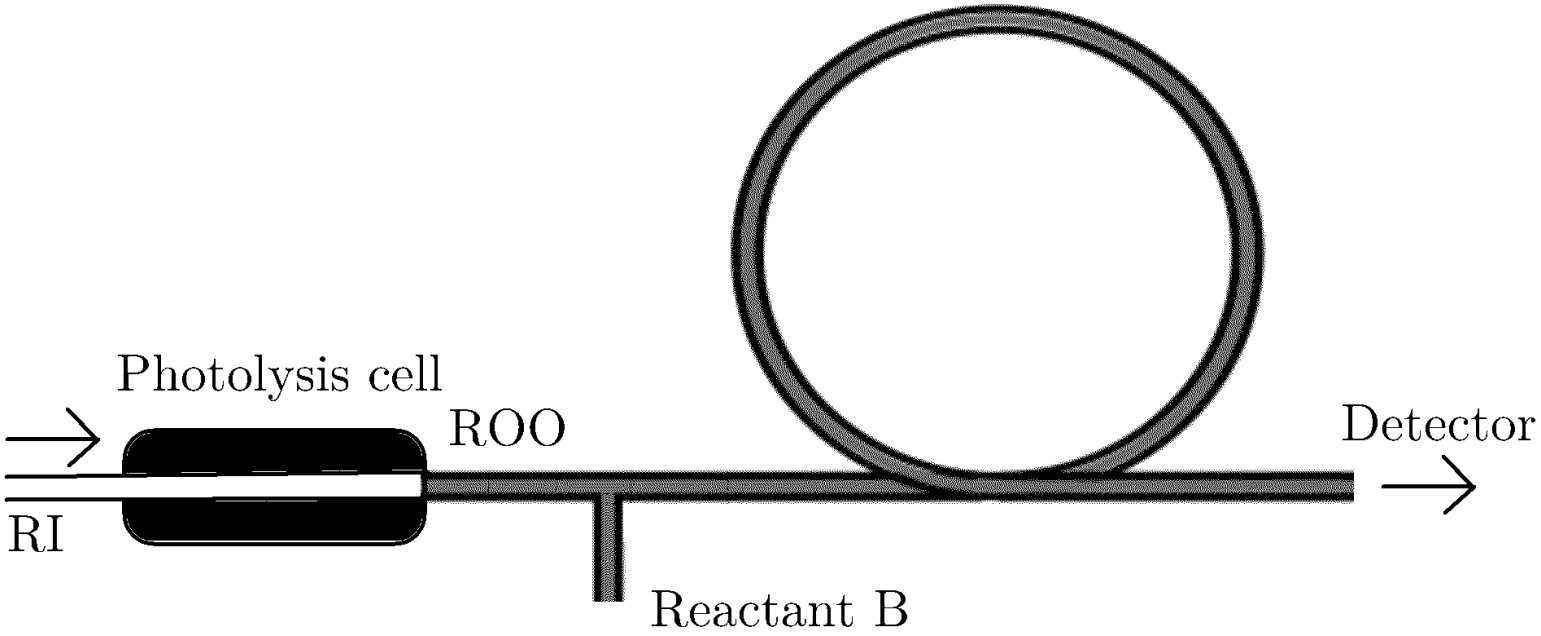
Less is more



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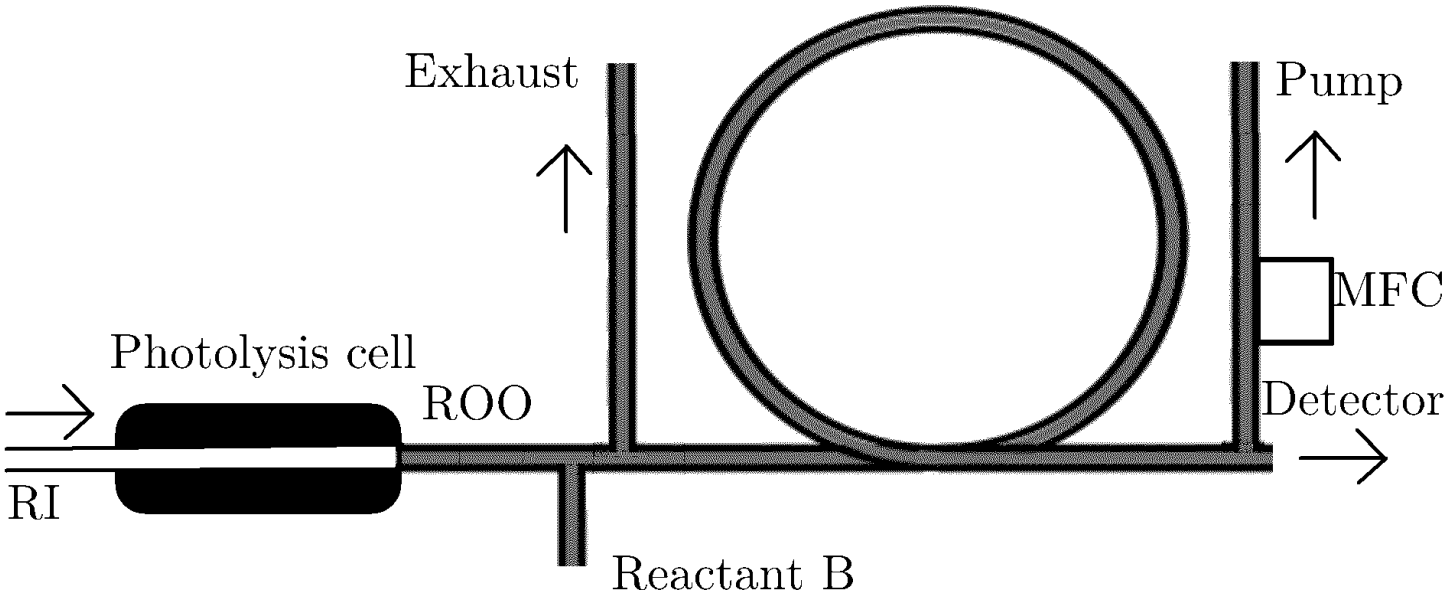

First study: surface uptake (Durif, Olivier et al., 2024, *JACS Au*)

- PFA
- Glass
- Stainless steel
- Copper
- Brass
- Aluminum

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Mass Spectrum

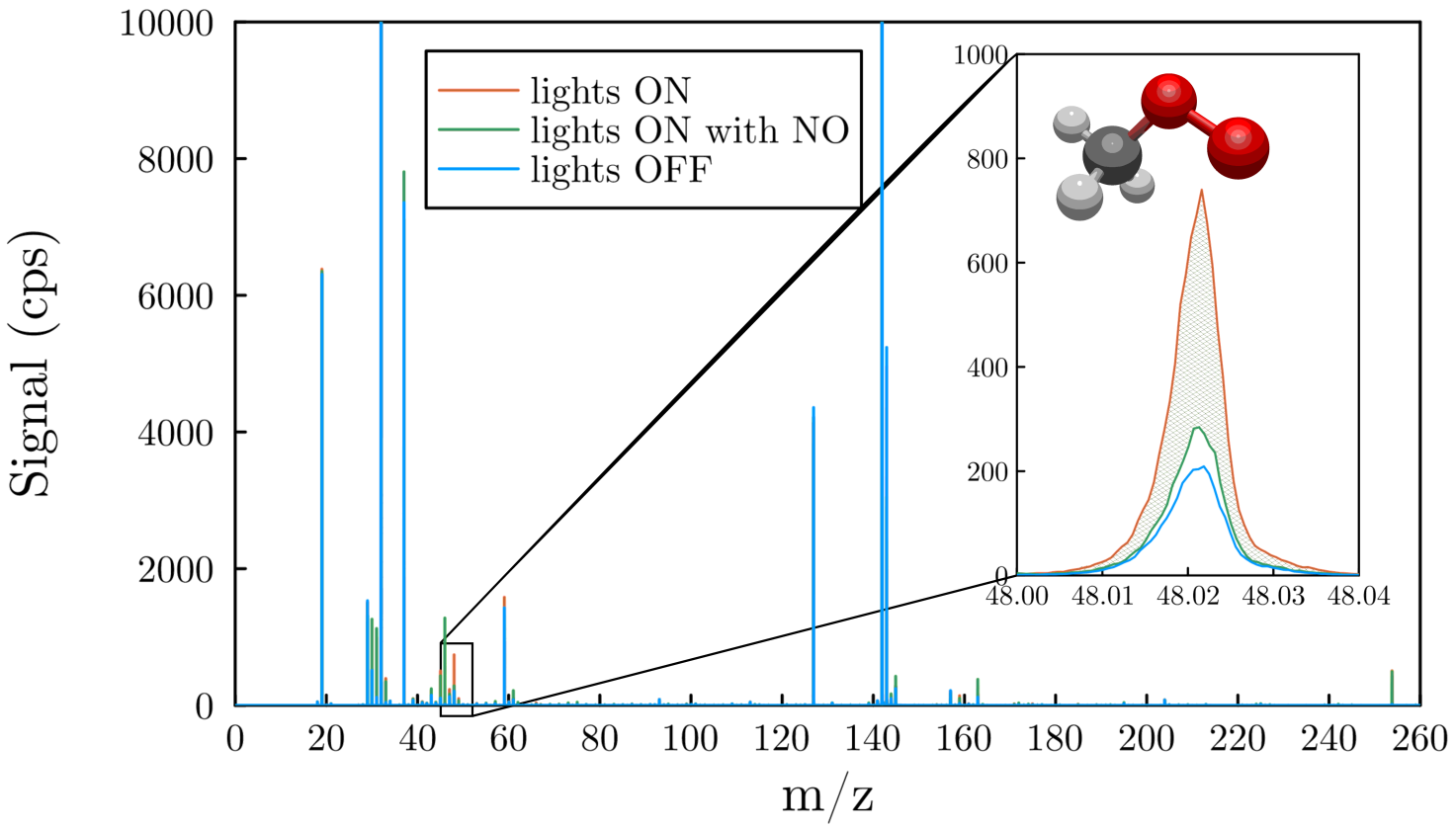

Figure: Detection of CH_3OO by proton-transfer-reaction mass spectrometry

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One kinetic point over the experiment time

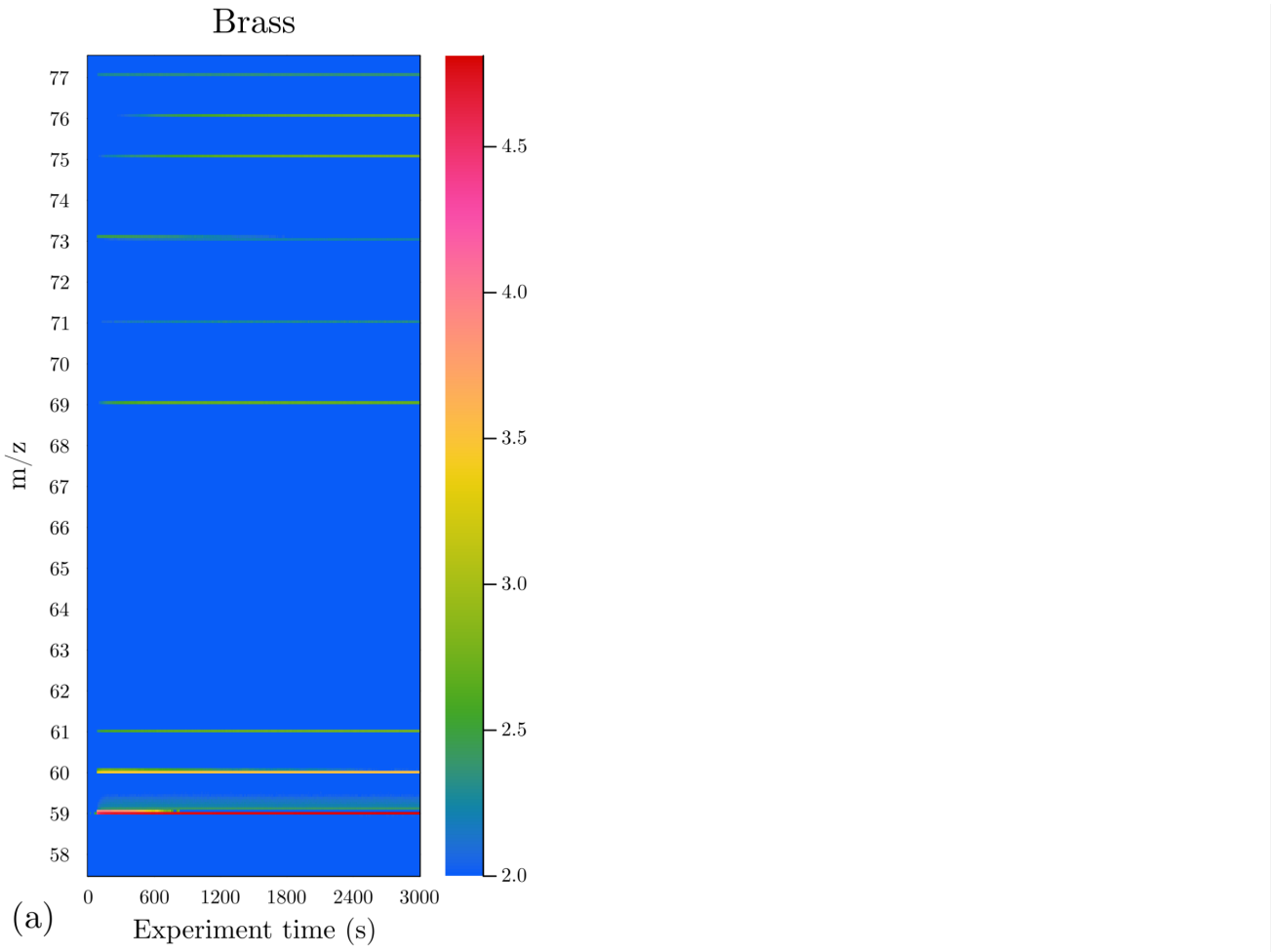

Figure: Time evolution of the mass spectra, after photolysis in the presence of a brass surface.

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One kinetic point over the experiment time

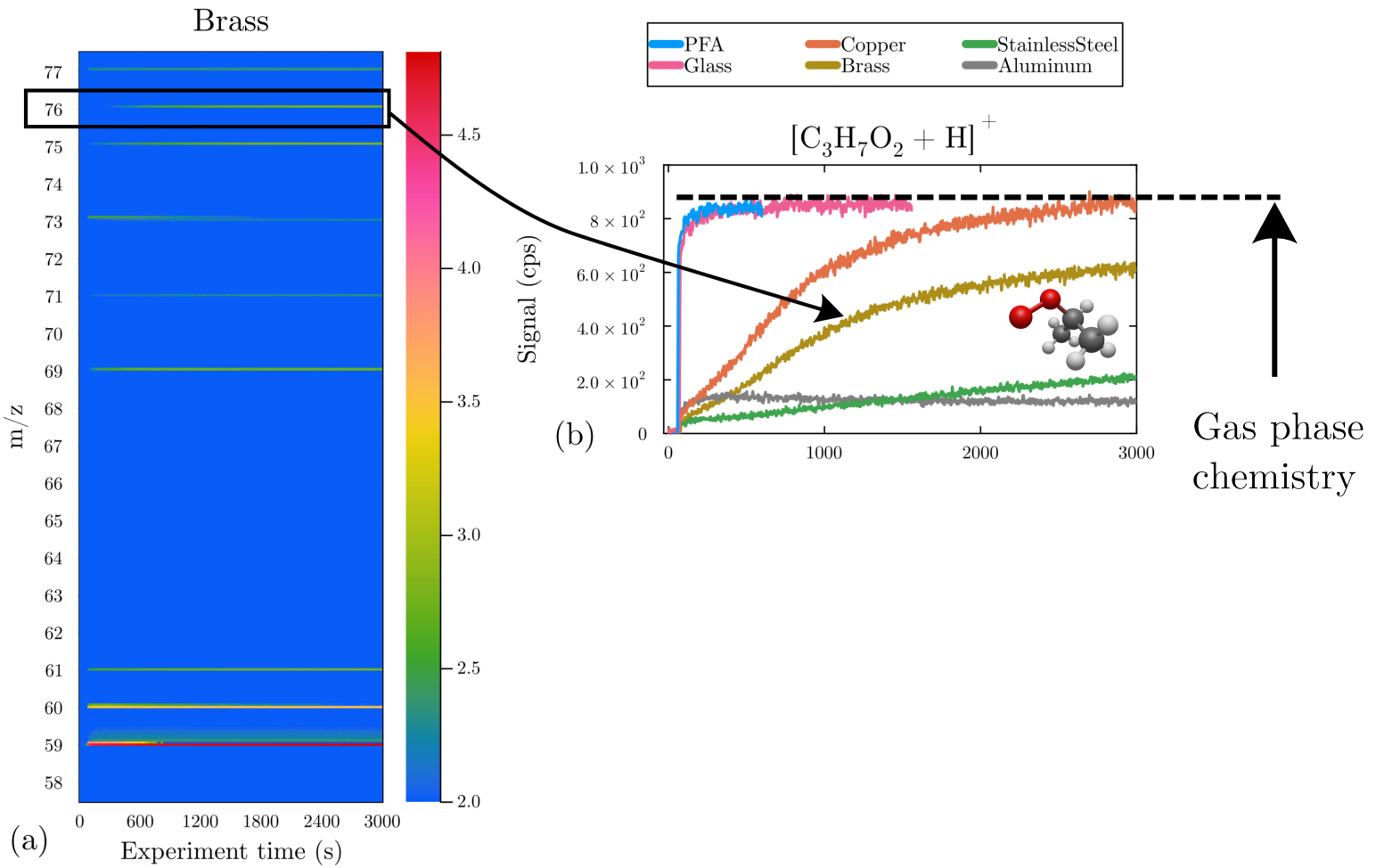

Figure: Time evolution of the mass spectra, after photolysis in the presence of a brass surface (left). Radical for various surfaces (right).

One kinetic point over the experiment time

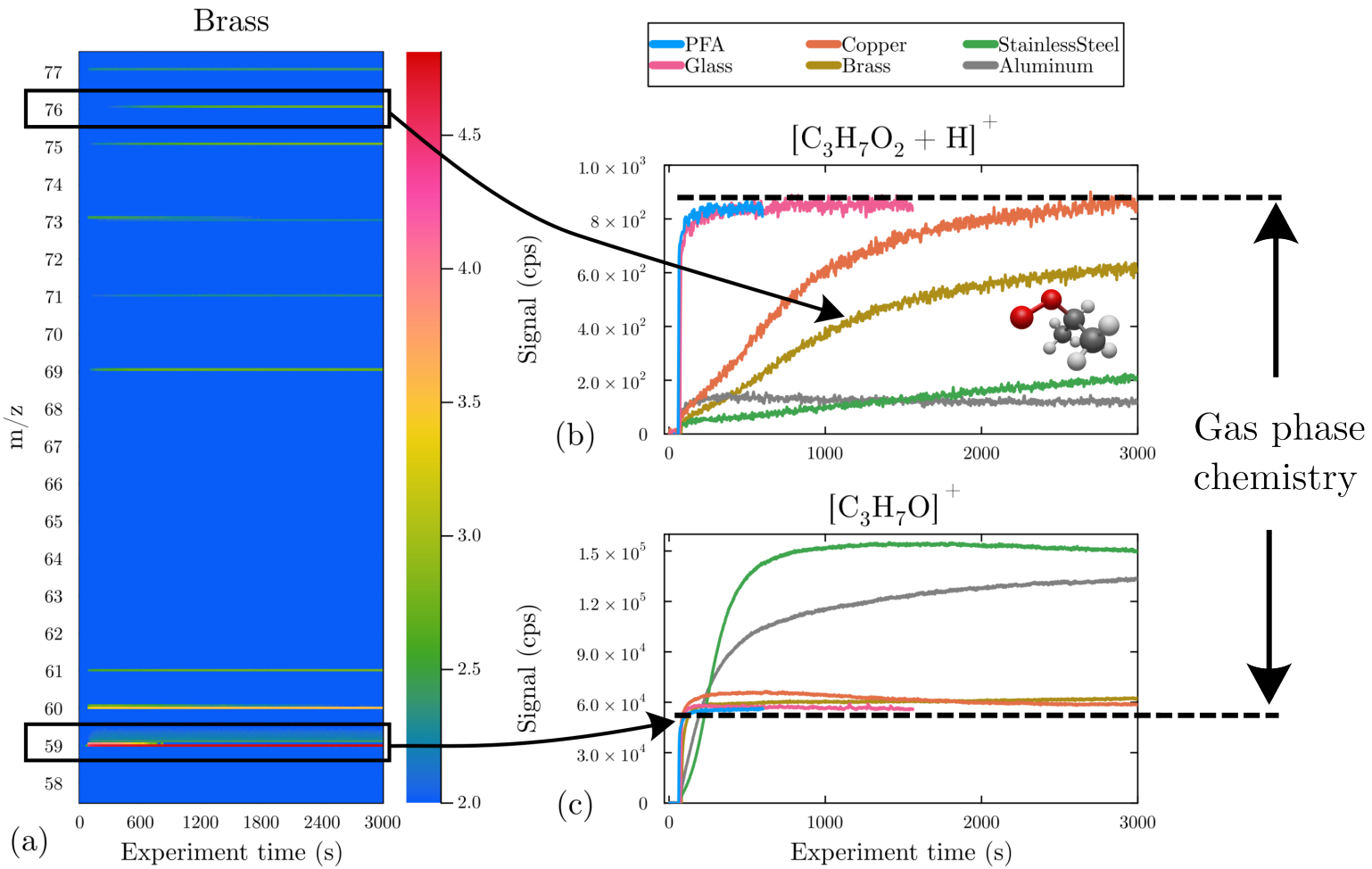

Figure: Time evolution of the mass spectra, after photolysis in the presence of a brass surface (left). Radical and main product for various surfaces (right).

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Uptake by surfaces

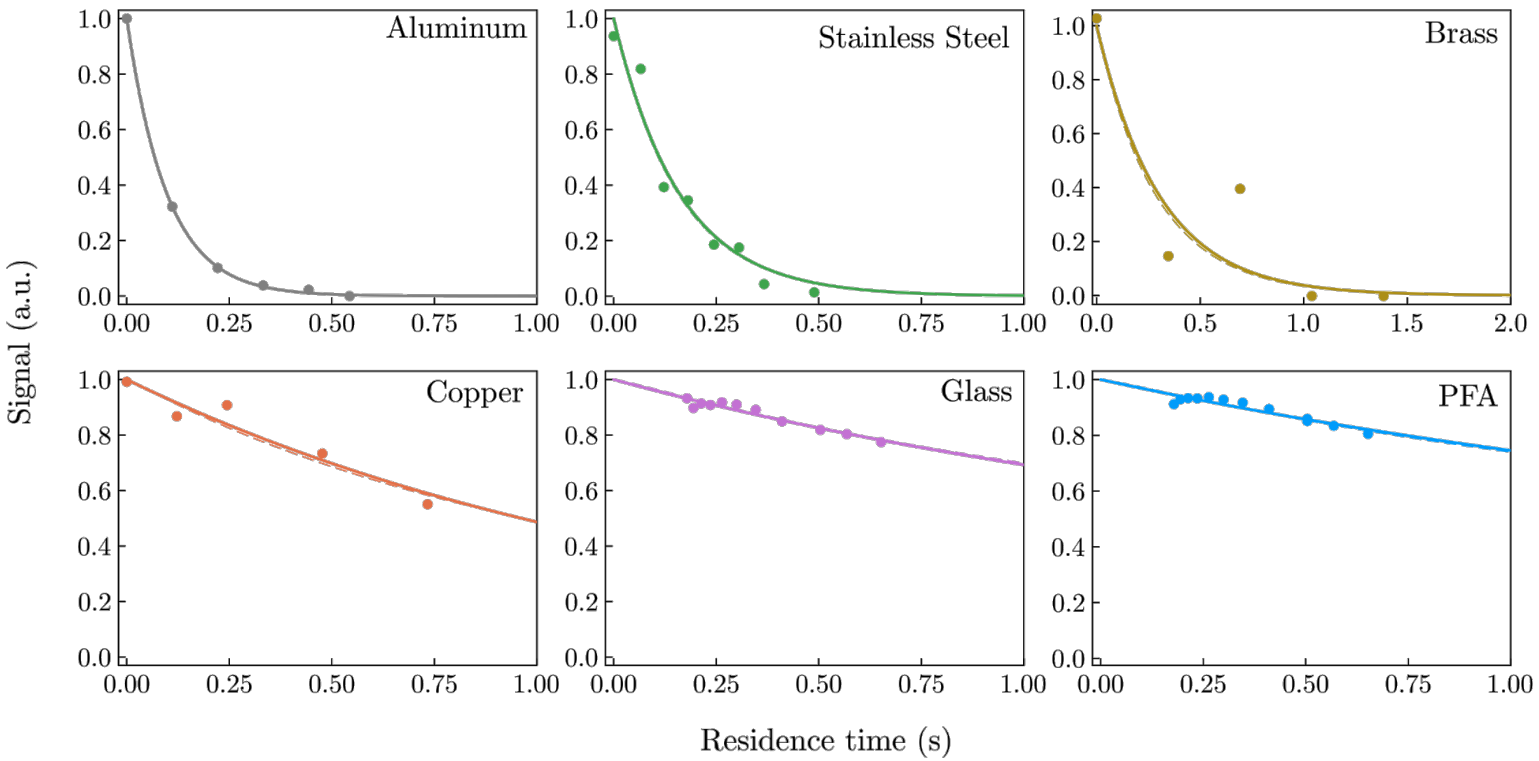

Figure: Decays of $CH_3OO^{\bullet}$ as a function of residence time with different surface materials.

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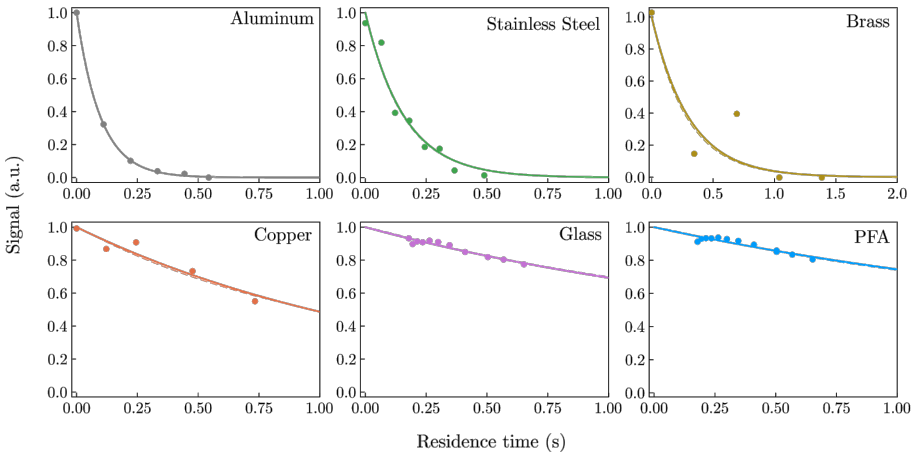

Chemical system:

$$\mathrm{ROO^\bullet} \xrightarrow{k_{wall}} \mathrm{P}$$

$$\mathrm{ROO^\bullet} + \mathrm{ROO^\bullet} \xrightarrow{k_{gas}} \mathrm{P_2}$$

One term for the gas phase, one term for surfaces:

$$\frac{\mathrm{d}[\mathrm{ROO^\bullet}]}{\mathrm{d}t} = -2k_{gas}[\mathrm{ROO^\bullet}] - k_{wall}[\mathrm{ROO^\bullet}]$$

Fit (neglecting $\mathrm{ROO^\bullet}$ gas-phase reactions):

$$[\mathrm{ROO^\bullet}](t) = [\mathrm{ROO^\bullet}]_0 \exp(-k_{wall}t)$$

or

$$[\mathrm{ROO^\bullet}](t) = \frac{k_{wall}\exp(-k_{wall}t)}{\frac{k_{wall}}{[\mathrm{ROO^\bullet}]_0} + 2k_{gas}\left(1 - \exp\left(-k_{wall}t\right)\right)}$$

All data on Zenodo, id: 8250035

Conclusion & Prospects

- A new experimental setup enables the direct and specific measurement of the simplest organic peroxy radicals in the laboratory ($CH_3OO^\bullet$, $C_2H_5OO^\bullet$, $C_3H_7OO^\bullet$, ...).

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- High uptake of peroxy radicals by metals, following the galvanic series (nobility of metals) and potentially competing with gas-phase reactions in laboratory installations.

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- Work in progress on PTR-MS data analysis and chemical kinetics to implement unsupervised learning (MassSpec.jl)

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- High uptake of peroxy radicals by metals, following the galvanic series (nobility of metals) and potentially competing with gas-phase reactions in laboratory installations.
- Work in progress on PTR-MS data analysis and chemical kinetics to implement unsupervised learning (MassSpec.jl)
- A versatile spectrometer, which has also been applied to laboratory measurements of non-exhaust traffic emissions

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Thank you for your attention