

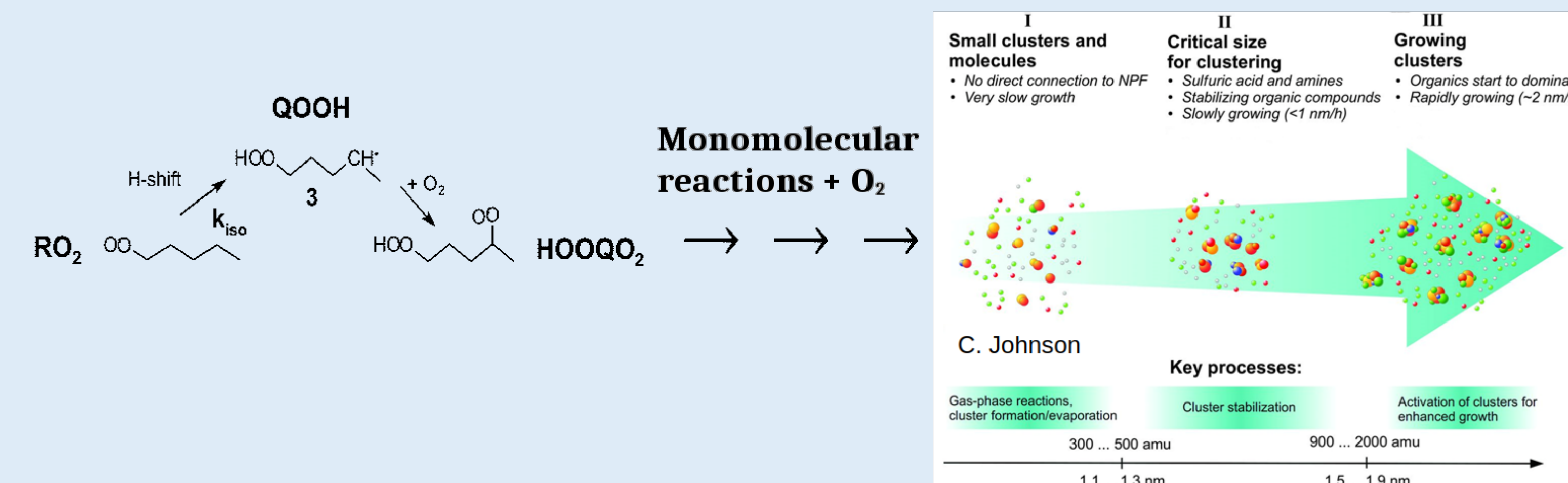
From RO₂ to HOMs: Investigating the monomolecular reactions of individual unsaturated RO₂ with Proton-Transfer-Reaction Mass Spectrometry

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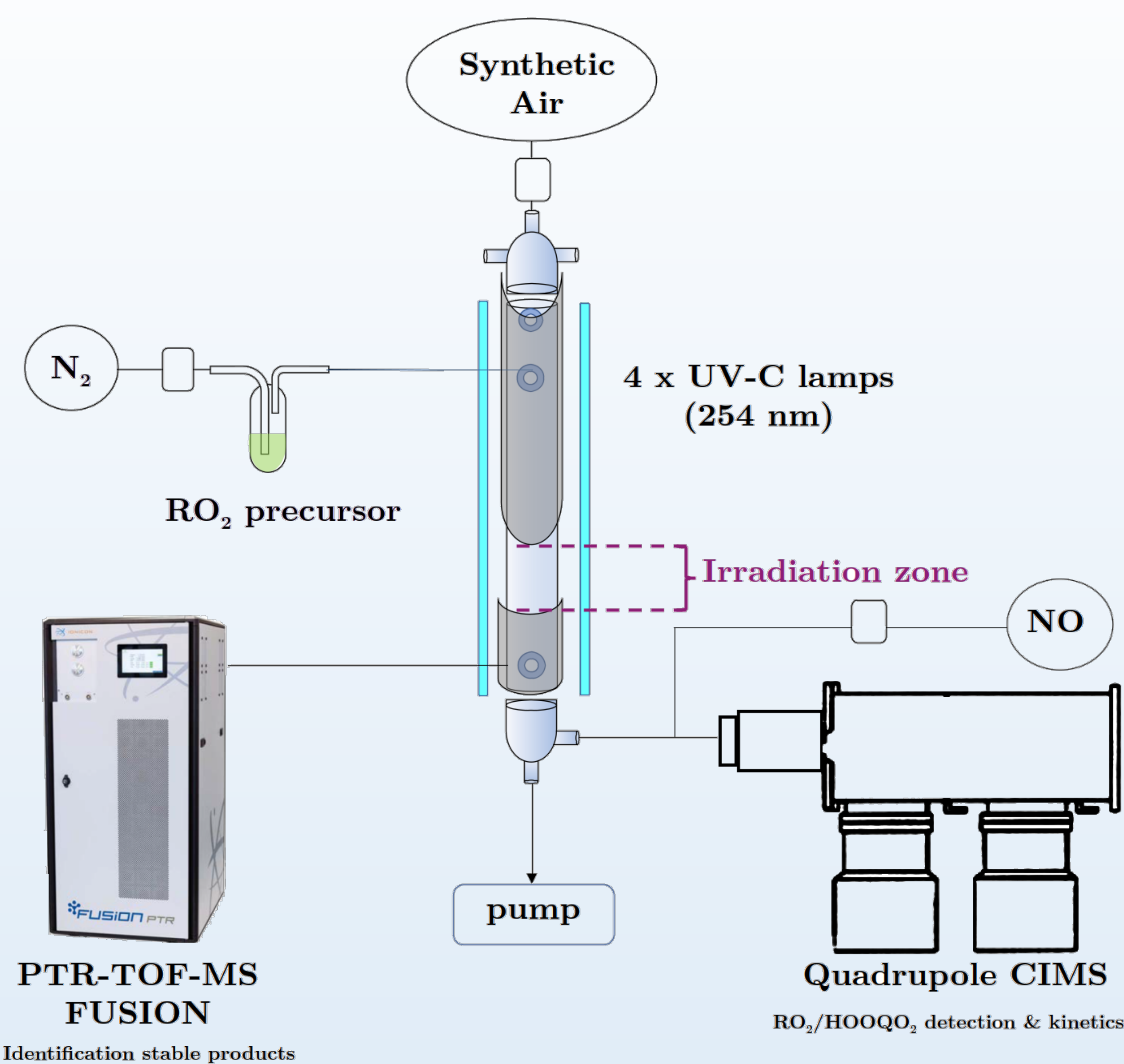
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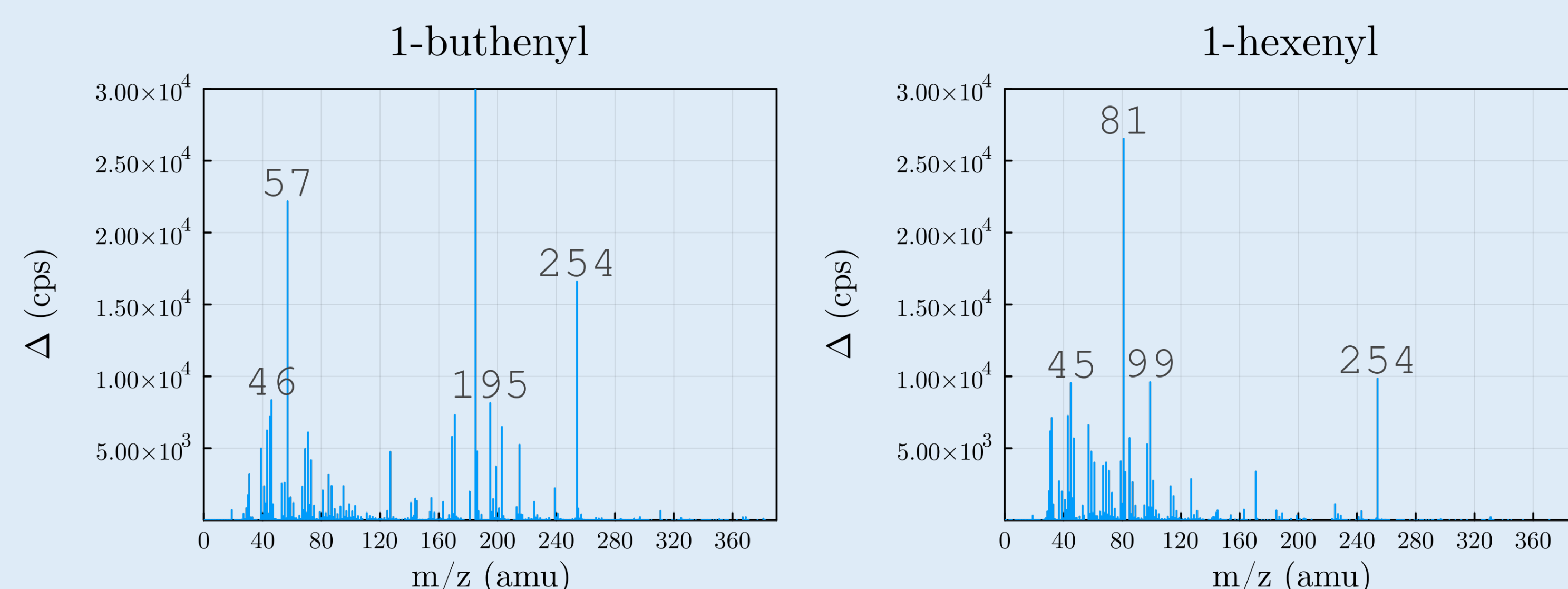
- Successive monomolecular reactions (autoxidation) of organic peroxy radicals (RO₂) leads to highly oxygenated, low vapor pressure compounds (HOMs), ultimately producing new organic particles.
- Structure-activity relationships (SARs) have recently been proposed for some of these reactions. But many other monomolecular pathways for the RO₂ remain to be quantified and experimental data is scarce.
- In this work, the monomolecular reactions (H-shifts, cyclisation) of unsaturated RO₂, relevant for instance for terpene oxidation, are studied theoretically and experimentally. Proton-Transfer-Reaction Mass Spectrometry is used to monitor both the radicals and stable products.



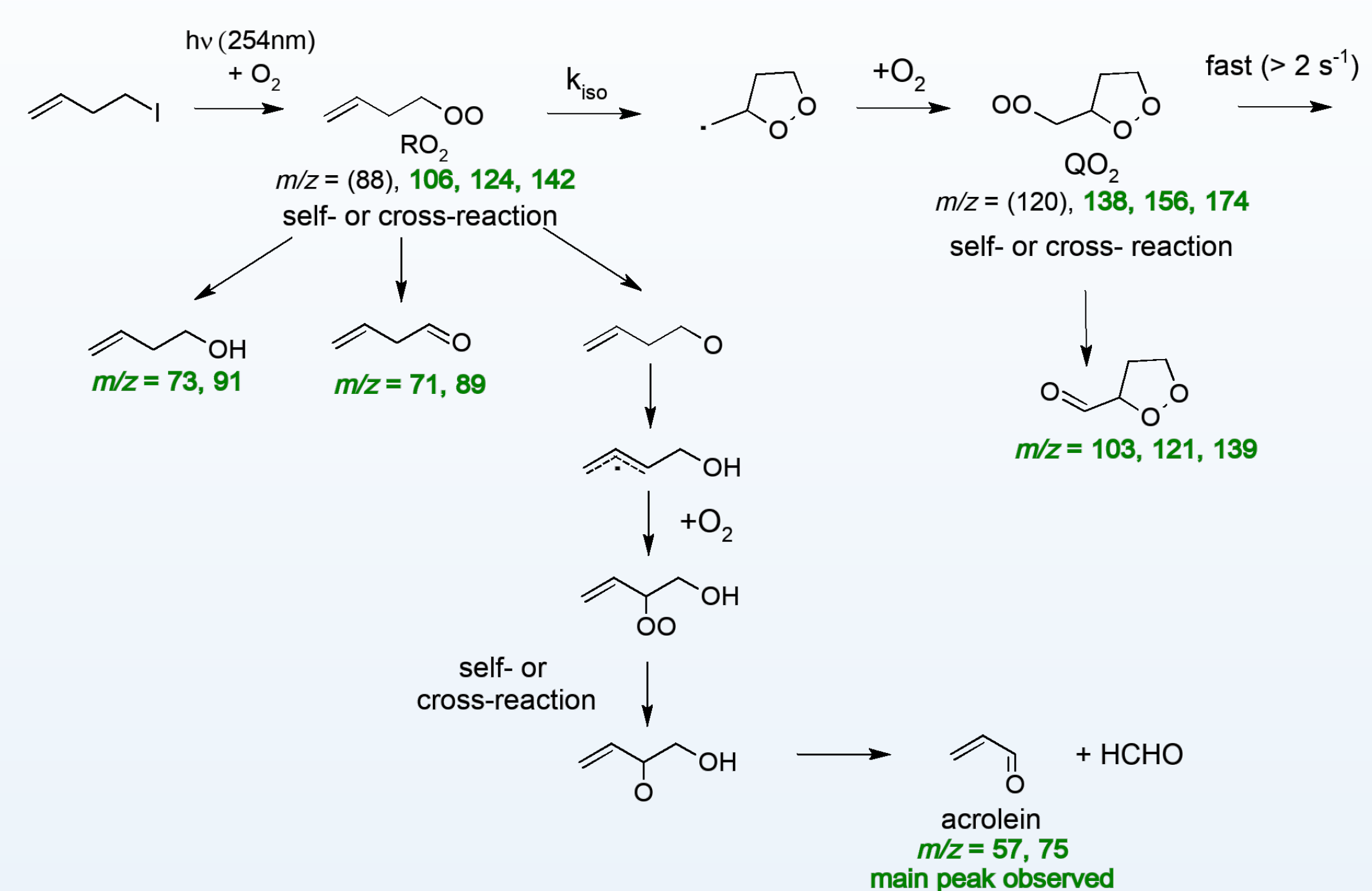
Experimental Setup



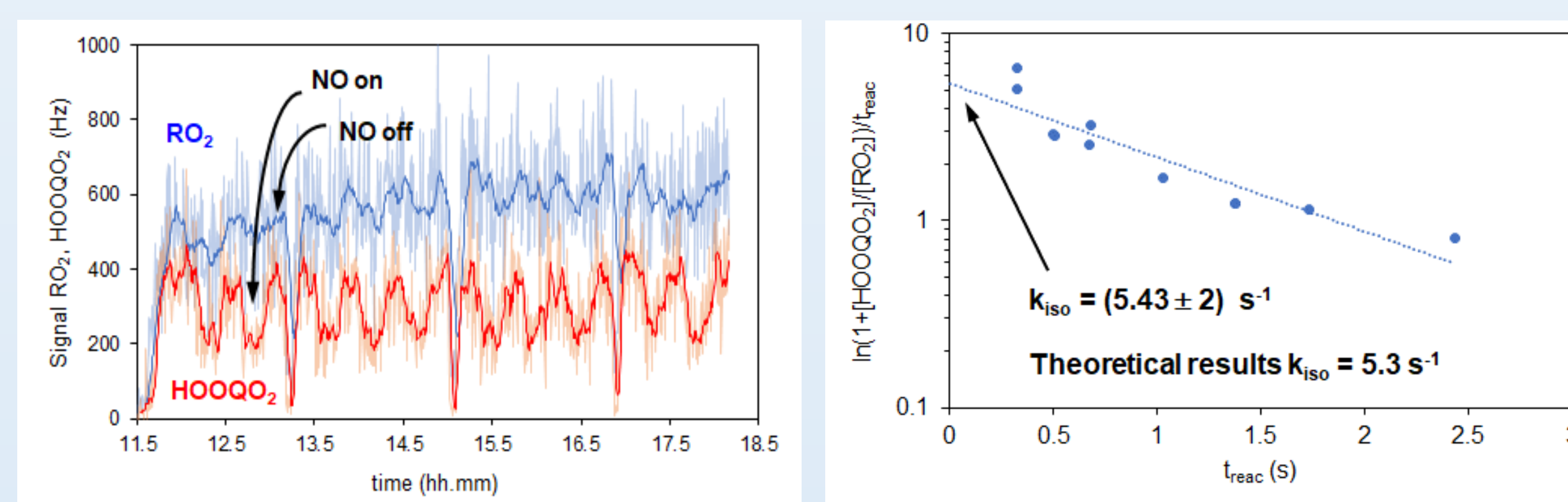
Subtracted Mass Spectra



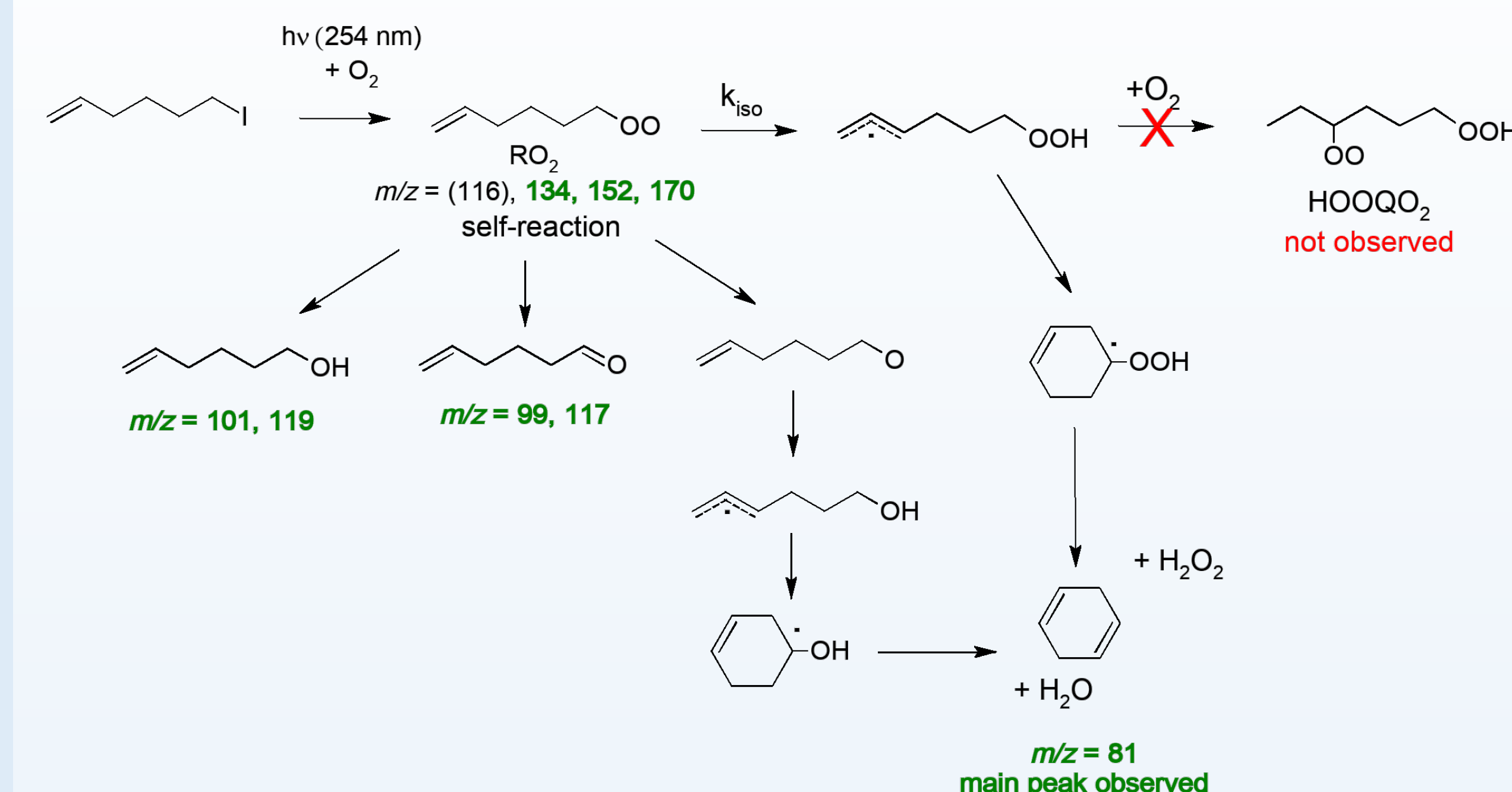
I. Isomerisation of 1-butenylO₂



Both RO₂ and HOOQO₂ detected with the CIMS
 Isomerisation rate from $\ln(1 + [HOOQO_2]/[RO_2])/t_{\text{reac}}$
 But HOOQO₂ also reacts away fast extrapolate to t=0sec

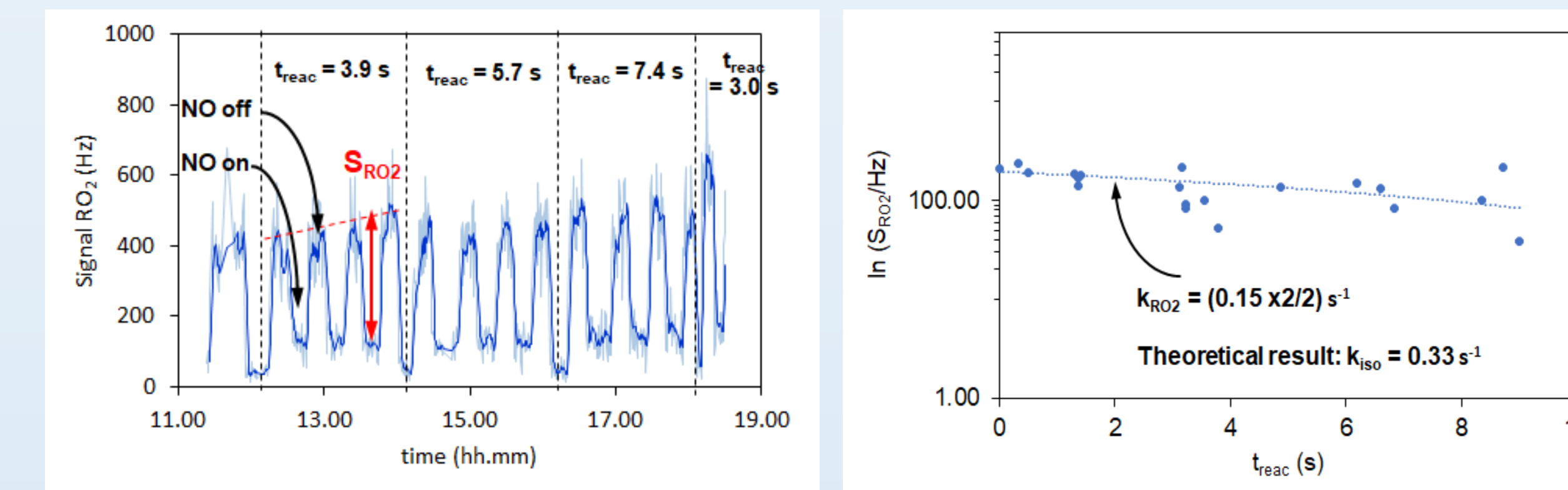


II. Isomerisation of 1-hexenylO₂



The observed ions revealed both expected and unexpected product channels. Decomposition in the alkoxy channels seem to be important.

Only RO₂ detected with the CIMS, not HOOQO₂
 HOOQO₂ reacts away fast (> 2 sec⁻¹)
 Isomerisation rate from observed RO₂ decay



Conclusion

Being able to monitor both RO₂ radicals and their stable products in individual reactions is essential to validate expected reaction channels and reveal unexpected ones. The chemistry of the initial steps leading to HOMs and new particles is complex and still requires more quantitative (kinetics) and qualitative experiments and theoretical calculations..

Acknowledgments

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