

Time-resolved Photochemistry of Organic Solutes in Aqueous Microdroplets



Engineering and Physical Sciences Research Council

in Aqueous Microdroplets



University of BRISTOL

Conlan Broderick
Supervisors:

Dr Bryan R. Bzdek, Prof Andrew J. Orr-Ewing & Dr Thomas A. A. Oliver

School of Chemistry, University of Bristol,
Cantock's Close, Bristol, BS8 1TS, UK

1. Background¹

The composition of the troposphere is controlled by a complex network of reactions involving **volatile organic compounds** (VOCs), which lead to the formation of **secondary organic aerosols** (SOAs). Organic aerosols comprise a significant proportion of atmospheric **pollution**, having a large effect on **population health** and the **global climate**.

Improvement in modeling the growth and processing of SOAs in the atmosphere is necessary for more accurate prediction and prevention. Understanding how certain photochemically active atmospheric compounds, such as **pyruvic acid**, react in **aerosol phases** is required. An aerosol system is a better representation of the tropospheric environment than the **bulk solution** in a lab, so directly studying the formation of SOAs and their photochemistry will **improve atmospheric models**.

- How do the **optical properties** of a droplet affect the **photochemistry** of PA, compared to reactions in the bulk?

- What are the **intermediates** and **excited states** that occur in a PA droplet and what controls their lifetime?

3. Key Questions to answer

4. Aims & Objectives

- Conduct bulk solution **fluorescence lifetime spectroscopy** measurements on PA, exploring the **intermediates** and **excited states** lifetimes.
- Probe droplets levitated in a linear quadrupole electrodynamic balance (**LQ-EDB**) with initial **coupling to TCSPC**.
- Vary the **environmental conditions** (pH and relative humidity) to measure the change in the photochemistry of PA.
- Assess the suitability of **transient absorption spectroscopy** coupled to the LQ-EDB to study PA droplets.

2. Pyruvic acid^{2,3}

Pyruvate acid, PA, is an **α -keto acid**. PA arises from a water soluble product of **isoprene** oxidation (a biological VOC, commonly emitted from trees). PA is:

- Environmentally-sensitive** and its chemistry will be pH dependent, especially in acidic aqueous conditions.
- Commonly used in atmospheric models, which do not consider **aqueous multi-phase data** that should be more representative of tropospheric chemistry shown in Figure 1.

Aerosols often exhibit several key differences to a bulk medium, such as:

- faster** reaction rates.
- lower** activation energies.
- high** surface area to volume ratios.
- super saturated** concentrations.

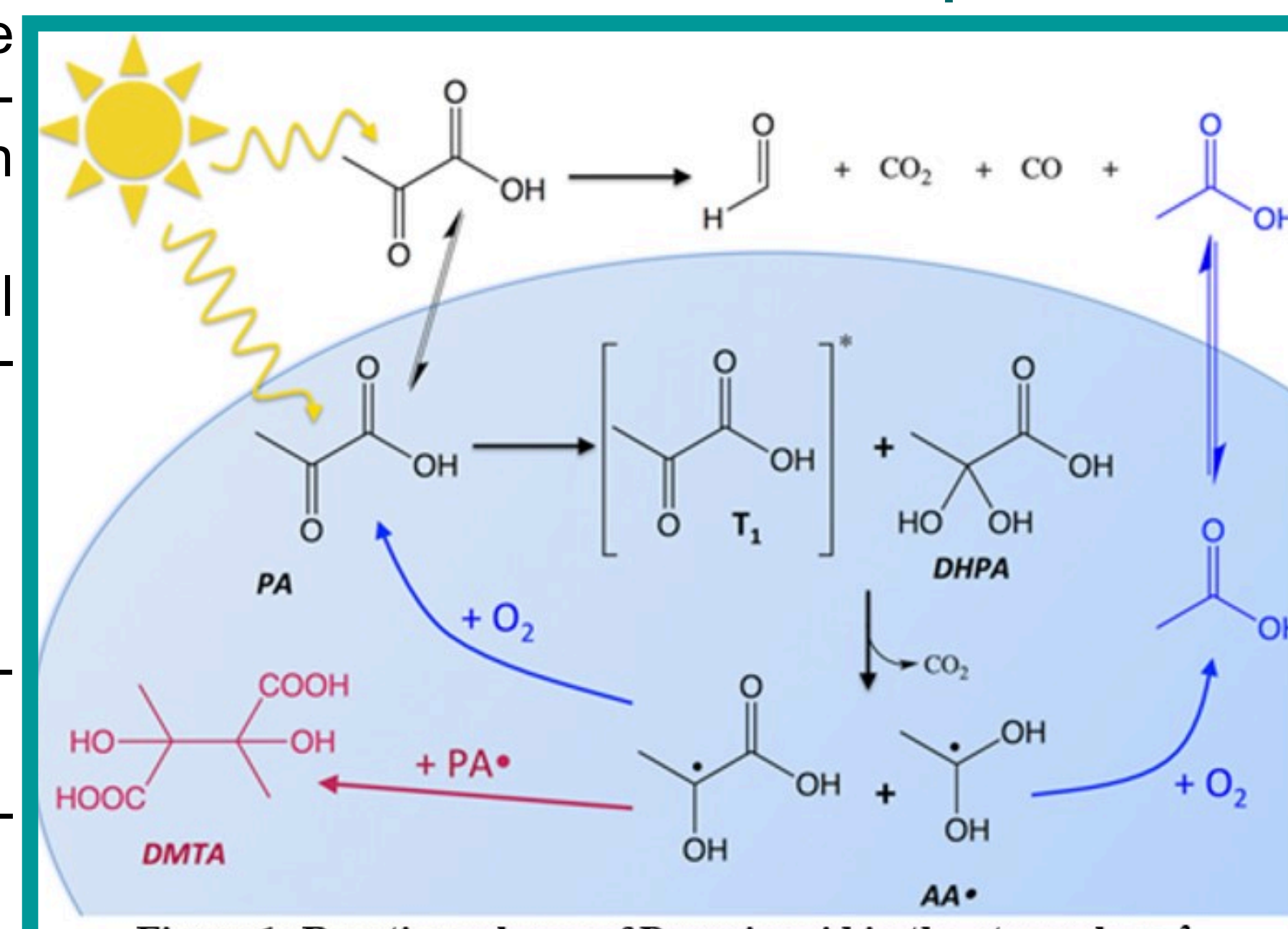


Figure 1: Reaction scheme of Pyruvic acid in the atmosphere.³

5. Levitating droplets⁴

An LQ-EDB apparatus, shown in Figure 2, coupled with a droplet dispenser will be used to create and **levitate charged microdroplets**. The quadrupole consists of four AC rods (two

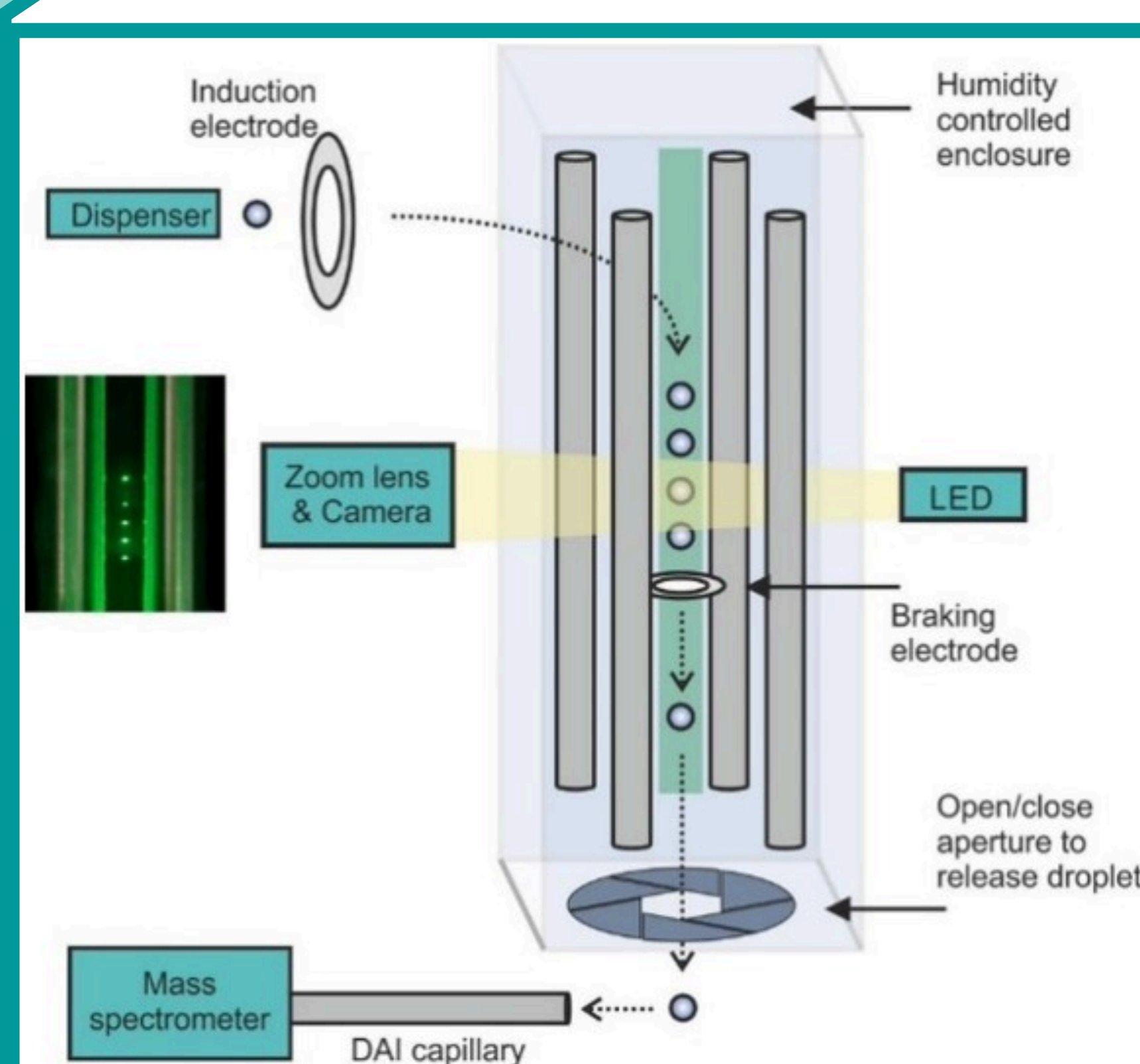


Figure 2: Basic diagram of the droplet levitation apparatus including the LQ-EDB, microdroplet dispenser and HD camera for phase function measurements. Provided by Dr Jim Walker

positive and two negative), with DC electrodes placed at the top and bottom of the central chamber. Droplets of **~30 nm diameter** will be generated using a **microdroplet dispenser**, then charged using an induction electrode, levitated and spatially confined in the electric field within the **quadrupole trap**. A green laser will illuminate the droplet so that the scattered light can be imaged on a camera and droplet size quantified by analyzing the **scattered light** (the phase function).

The strategy to couple an existing TCSPC setup with the LQ-EDB is yet to be confirmed, but requires access to a laser beam to **excite fluorescence**, and collection optics to transfer emitted photons to the detector. Adaptations to the current design of levitating droplet apparatus will be required to achieve objectives 2 & 4.

6. Spectroscopy techniques

Time-correlated single photon counting (TCSPC) works by exposing a sample to a UV or visible laser pulse to excite the sample by **absorption**. Then, a detector collects photons emitted by the sample and records their time delays after the laser excitation pulse. The time between the **excitation** and **fluorescence** is measured by an avalanche photodiode over multiple laser pulses; for each pulse, the timing electronics record the times for **photon emission**, which are then converted into a **histogram** after data collection over a large number of excitation laser pulses.⁵

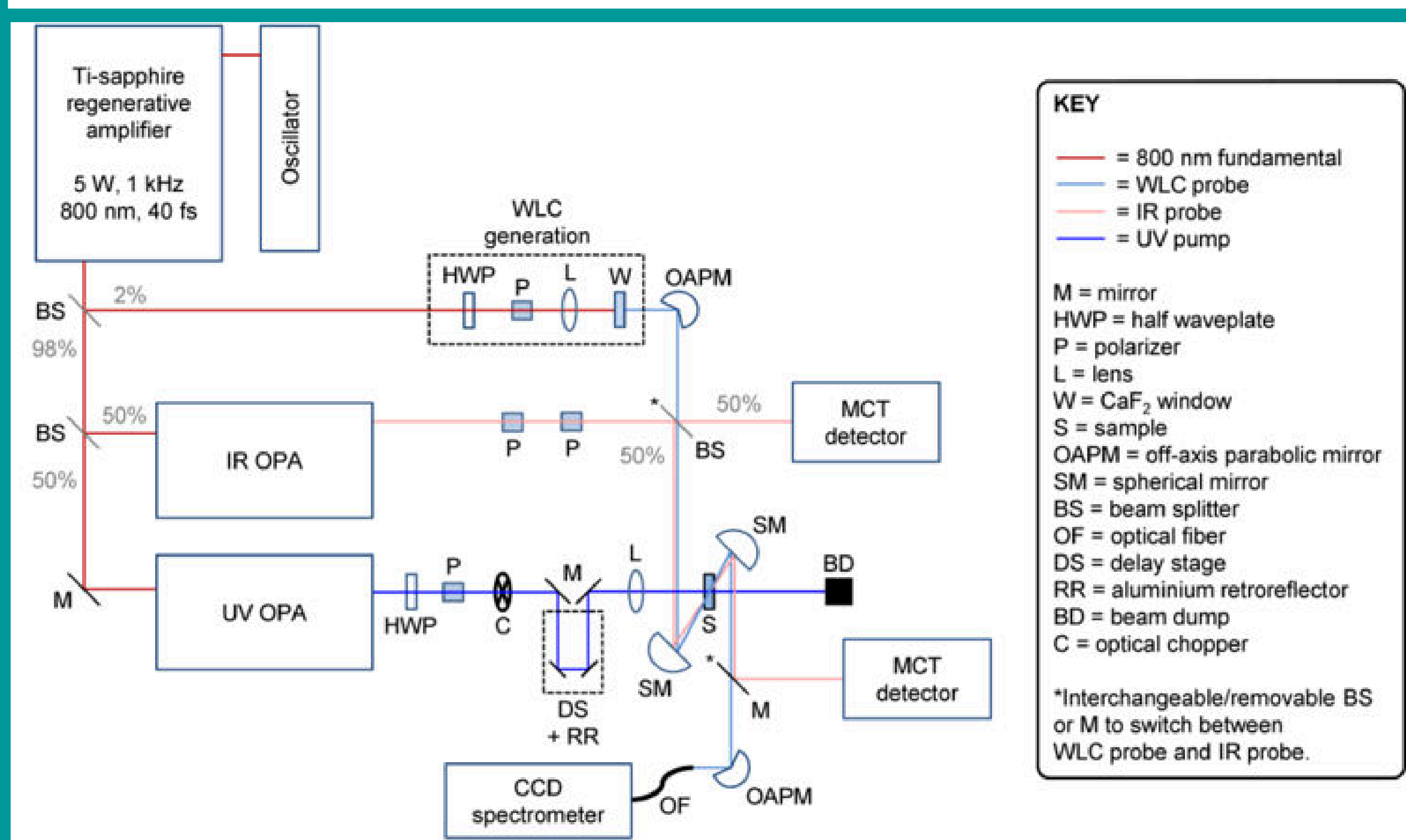


Figure 3: Schematic diagram of the ultrafast transient absorption spectroscopy setup at the University of Bristol.⁶ The inset key identifies the components of the experiment.

Transient absorption spectroscopy, shown in Figure 3, will be used to observe the population of the short-lived excited states of those intermediate molecules prepared by **photoexcitation**. Using a laser pump and probe experiment, transient absorption spectra will be obtained. The absorption of different wavelengths by the sample over time will distinguish different intermediates and products of the photo-excited sample. Two types of spectroscopy will be employed, transient electronic absorption spectroscopy (**TEAS**) and transient vibrational absorption spectroscopy (**TVAS**), where each employs different broadband spectra to resolve a range of chemical information.⁶

7. Challenges

- Challenge 1** - Developing a robust, reliable and repeatable method for measuring fluorescence or transient absorption spectra of a levitating droplet.
- Challenge 2** - New experiments will be likely to require custom-written software (written in LabVIEW, Matlab, or Python) to collect, process and analyse the experimental data.

8. Responsible Innovation

An improved understanding of atmospherically significant molecules that may contribute to issues of **global health and climate change**. Any research into human activity on climate is especially relevant due to the global consequences. An aspect of **interdisciplinary research** will be needed in this project to bridge the physical and environmental areas.

9. References

- Tarun Gupta, Pradhi Rajeev, and Rashmi Rajput, *ACS Omega* 2022 7 (2), 1575-1584
- X. Yan, *International Journal of Mass Spectrometry*, 2021, 468, 116639.
- A. E. Reed Harris, A. Pajunoja, M. Cazaunau, A. Gratien, E. Pangui, A. Monod, E. C. Griffith, A. Virtanen, J.-F. Doussin and V. Vaida, *J. Phys. Chem. A*, 2017, 121, 3327-3339.
- R. K. Kohli and J. F. Davies, *Anal. Chem.*, 2021, 93, 12472-12479
- W. Becker, *Advanced Time-Correlated Single Photon Counting Techniques*, SC, Berlin, Heidelberg, 2005, vol. 81, 11-25
- G. M. Roberts, H. J. B. Marroux, M. P. Grubb, M. N. R. Ashfold and A. J. Orr-Ewing, *J. Phys. Chem. A*, 2014, 118, 11211-11225