Time-resolved Photochemistry of Organic Solutes in Aqueous Microdroplets

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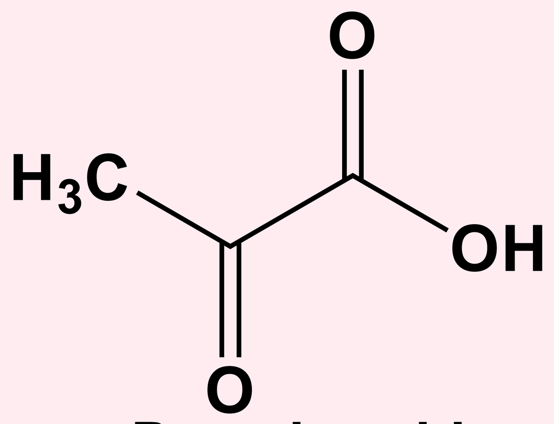
Background

- In the troposphere, **secondary organic aerosols** (SOAs) are a large proportion of organic aerosols, which contribute to global warming & climate change.[1]
- **Pyruvic acid** (PA) is an environmentally sensitive compound, which has a role in SOAs formation.[2]
- PA chemistry in the **gas phase**, aqueous **bulk**, and at the **surface interface**, is uniquely different.[3]



Pyruvic acid

Key Questions

- What are the **excited states lifetimes** that occur in PA droplets?
- How do the **optical properties** of a droplet affect the **photochemistry of PA,** compared to reactions in the bulk?
- How do the **surface effects** change the photochemistry of PA?

Aims & Objectives

1. Conduct bulk solution **fluorescence/absorption lifetime spectroscopy** measurements on PA, exploring the **intermediates** and lifetimes of **excited states**.
2. Levitate droplets in a linear quadrupole electrodynamic balance (**LQ-EDB**) with initial **coupling to Time-correlated single photon counting**.
3. Vary the **environmental conditions** (pH & relative humidity) to measure the change in the photochemistry of PA.
4. Assess the suitability of **transient absorption spectroscopy** coupled to the LQ-EDB to study PA droplets.

TCSPC

Time-correlated single photon counting (TCSPC) exposes the sample to a UV or visible laser pulse to insight **excitation** and **fluorescence.** PA is excited at **345 nm** (within UVA range).

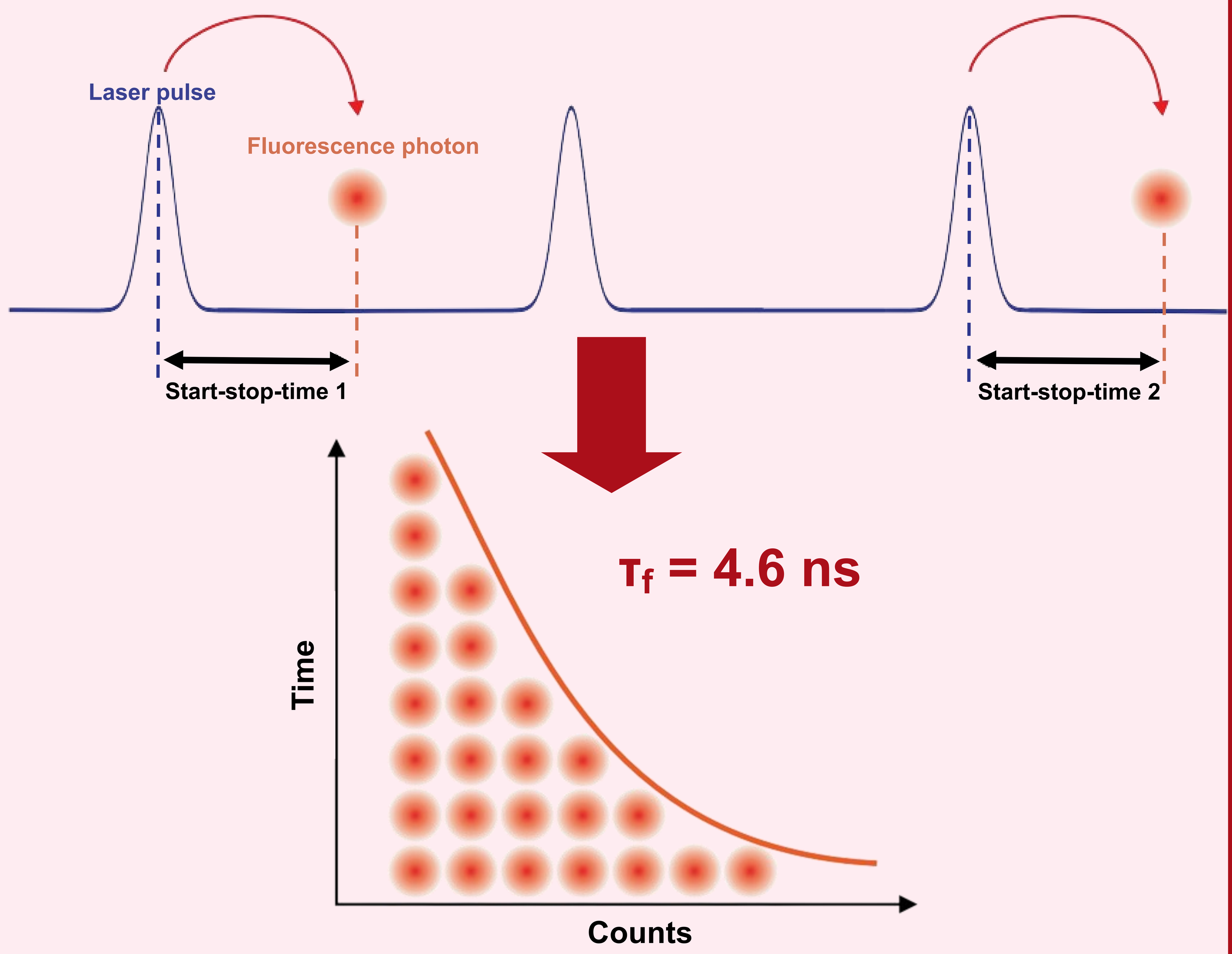


Figure 1: A pictorial representation of TCSPC and the histogram produced of the florescence decay from which a time constant is established.[4]

TAS

Transient absorption spectroscopy (Figure 3) is used to observe the population of the short-lived excited states (a few femtoseconds) to long-lived photoproducts (a few nanoseconds) after **photoexcitation**.

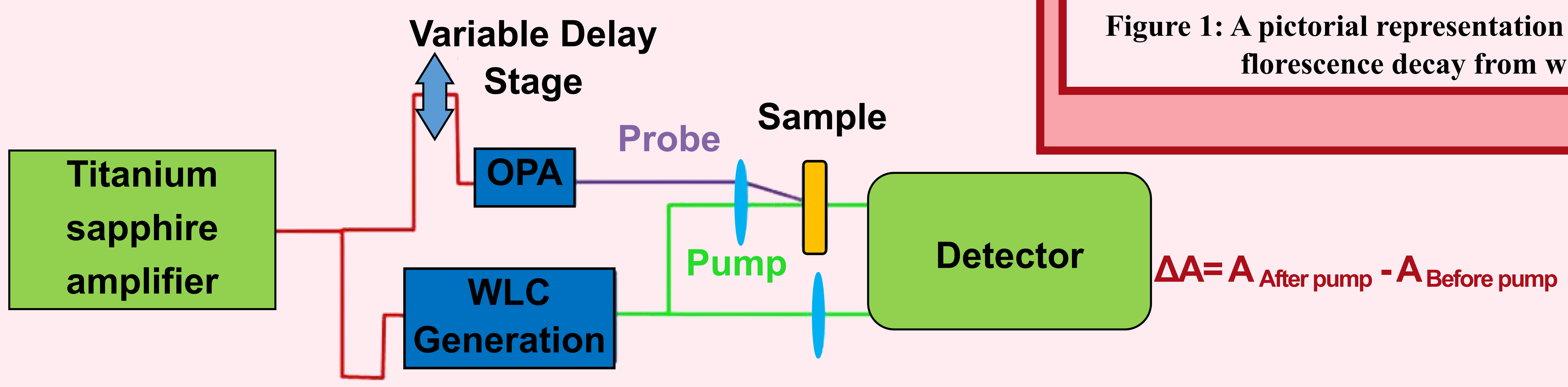


Figure 2: A schematic of the Pump Probe setup of TAS.[5]

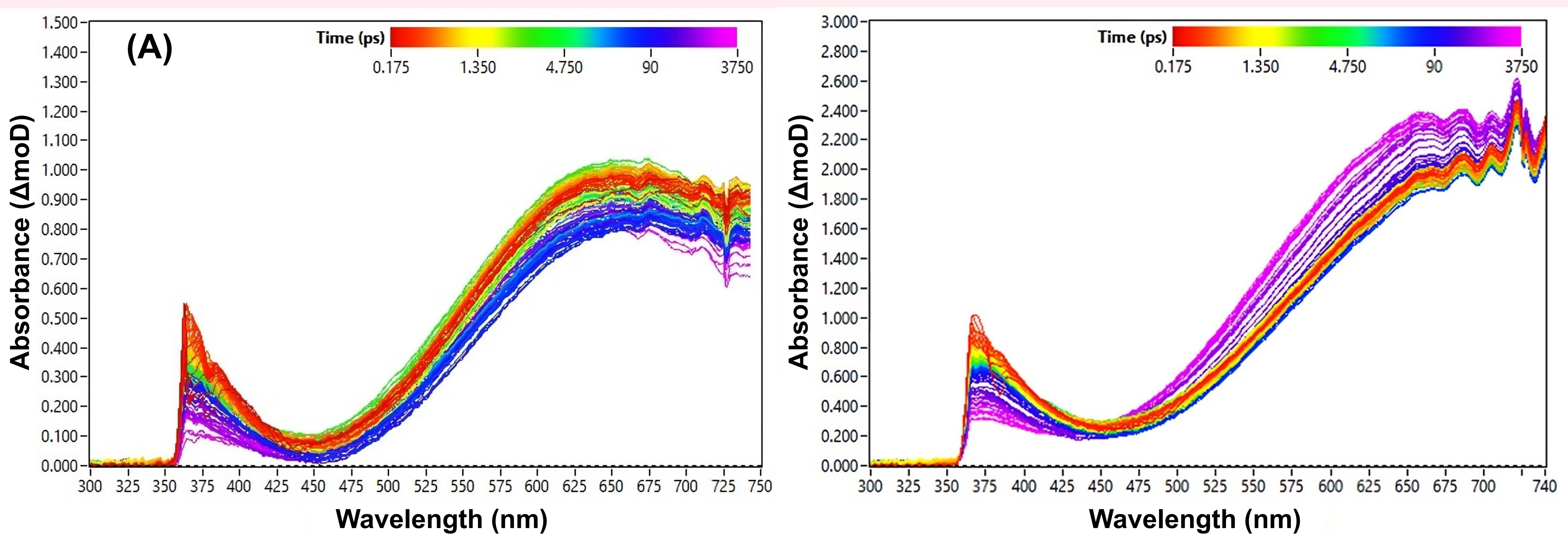


Figure 3: Transient Absorption spectra at 345 nm; (A) PA 1 molar in water, (B) PA 2 molar in water with 250 µm path length.

Future Work

TCSPC setup coupled with the LQ-EDB will allow for the individual droplets to be excited and retrieve the fluorescence of the droplets to compare to the bulk solution.

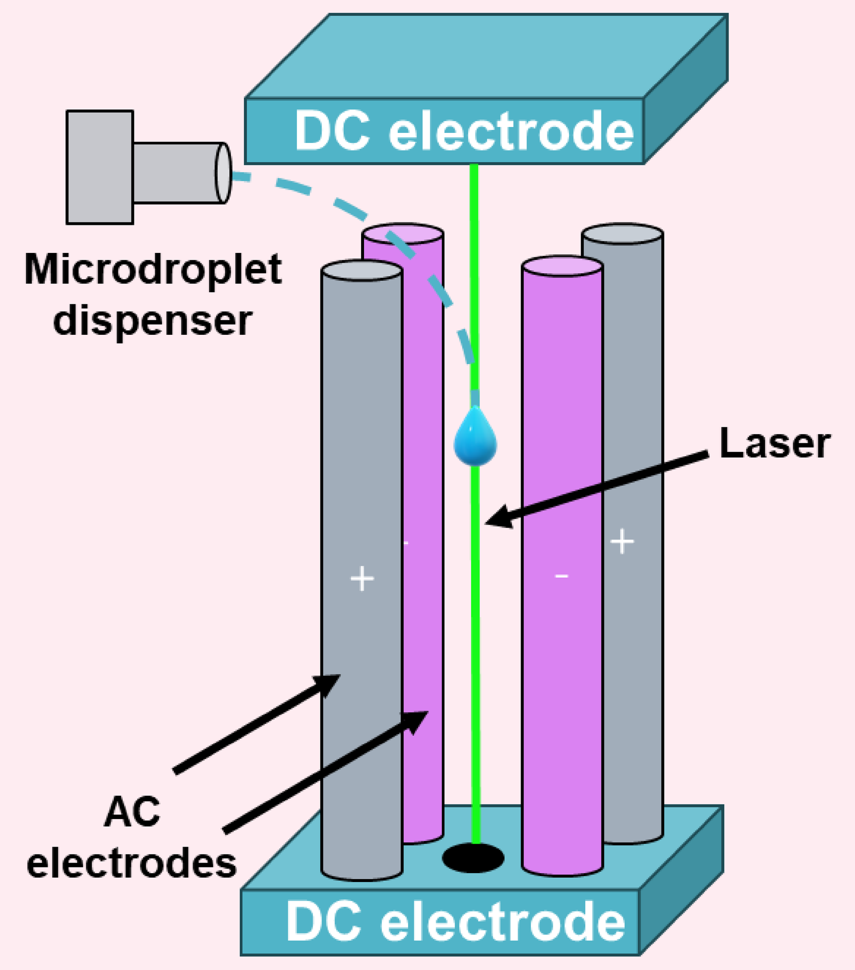


Figure 4: Schematic of the LQ-EDB.

References

1. Tarun Gupta, Pradhi Rajeev, and Rashmi Rajput, ACS Omega, 2022, 7(2), 1575-1584
2. X. Yan, *International Journal of Mass Spectrometry*, 2021, 468, 116639.
3. 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.
4. M. Wahl, PicoQuant, Time-Correlated Single Photon Counting, 2009.
5. Central laser facility, 2019, hpttps://www.clf.stfc.ac.uk/Pages/-200-fs-Transient-Absorption-(350-1600-nm)-Spectroscopy.aspx. Accessed: 12/04/2024.