Development of a Novel Single Droplet Mass Spectrometry Approach to Investigate Interfacial Photochemistry in Aerosol Droplets

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Sea spray aerosol; effects and composition

- **Large uncertainties in cloud-aerosol interactions on radiative forcing in our atmosphere presents a need for an improved understanding of aerosol effects**
- **Around 70% of the earths surface is covered by ocean which produces 2000-10000 Tg/yr of sea spray aerosol (SSA) [1]**
- **5-15 Tg/yr of organic material is contained within this SSA[1]**
- **Two-thirds of the fatty acid content of SSA is palmitic acid and steric acid [2]**

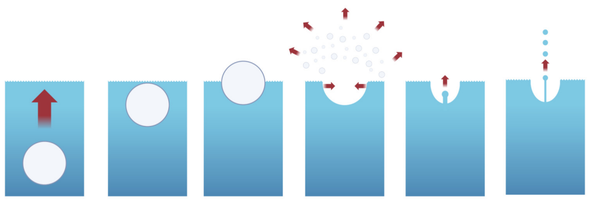


Figure 1. Mechanism for SSA generation

Why do we need this instrument?

1. **These surface-active organics can have surface tension lowering effects, altering activation of SSA which can act as cloud condensation nuclei (CCN) [3]**
2. **Surfactants at the surface can undergo important, but understudied accelerated photochemical reactions at the interface when compared to the bulk [4]**
3. **Reactions with photosensitizers and light along with gases in the atmosphere including ozone cause breakdown of organics like palmitic acid into a range of products with differing properties[5]**
4. **The breakdown can affect many properties of SSA including lifetime, activation and optical properties**

What sort of instrument is needed?

To probe these reactions an instrument that can isolate the surface and identify the constituent molecules is needed

Mass spectrometry – provides high resolution approach to detect small concentrations of organic molecules

Field induced droplet ionisation (FIDI) – Single droplet atmospheric ionisation approach that samples the surface of droplets via a very large electric field.

1. Perform FIDI on falling droplets

- **The first step of the instrumental development process is to perform FIDI on free falling droplets**
- **Using larger droplets, ~200µm in diameter, with reduced surface tension (<40 mN/m) will be good candidates for the first attempts**
- **This phase of development is completed once droplets closer to 80µm in diameter have been reached.**
- **Going smaller requires more control over the droplet.**

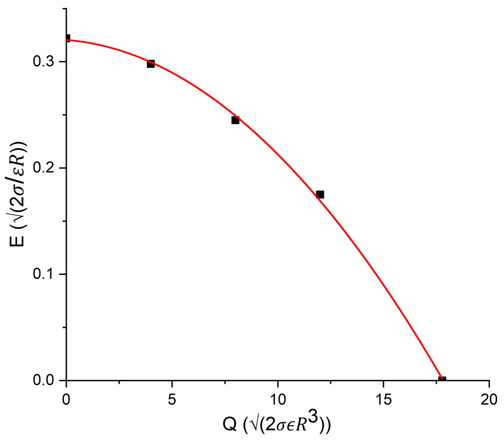
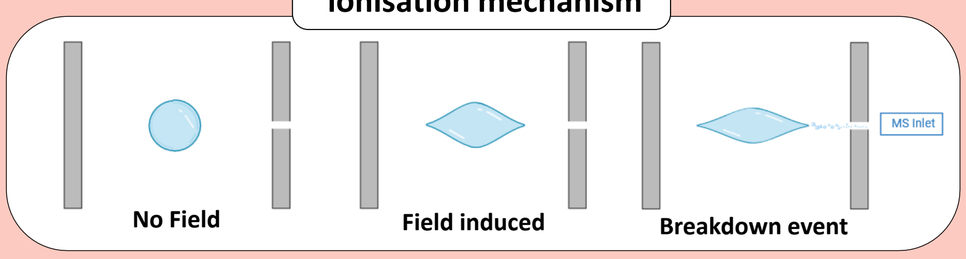
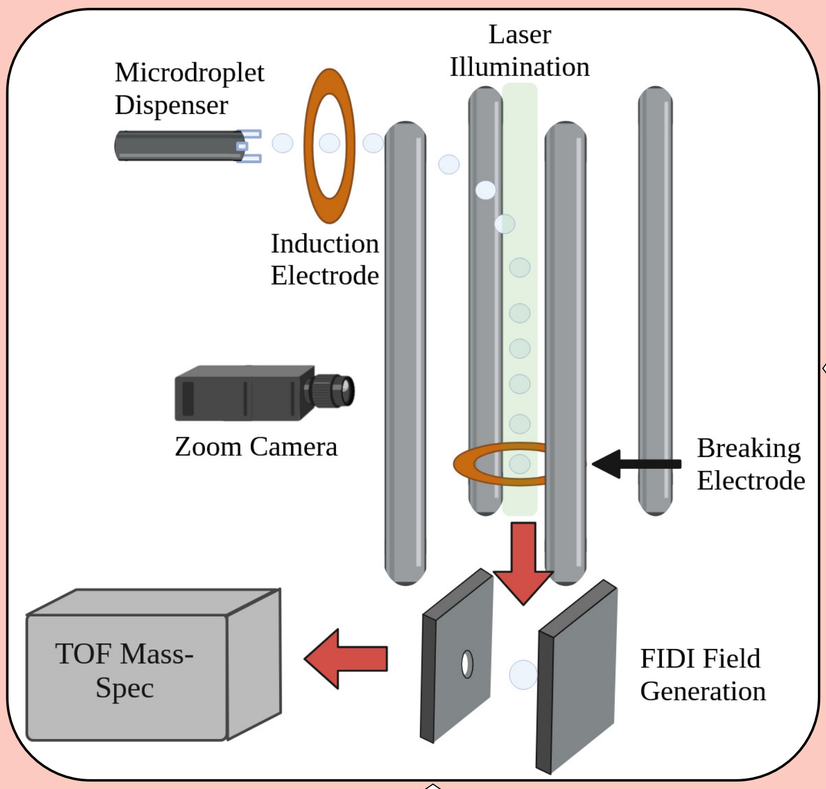


Figure 2. The field strength required to ionize the droplets can be calculated if a few characteristic parameters are known; Surface tension at the droplet interface, radius of droplet, amount of charge on the droplet [6]

Field-induced droplet ionisation mechanism





2. Couple FIDI with linear quadrupole

- **The second phase consists of coupling the FIDI source to a linear quadrupole electrodynamic balance (LQ-EDB) to control the dispensed droplets**
- **This will allow the charged droplets to be trapped and released into the FIDI source when required**
- **During trapping the droplets can be evaporated to consolidate charge and move to smaller sizes, also allowing photochemical reactions to be performed**

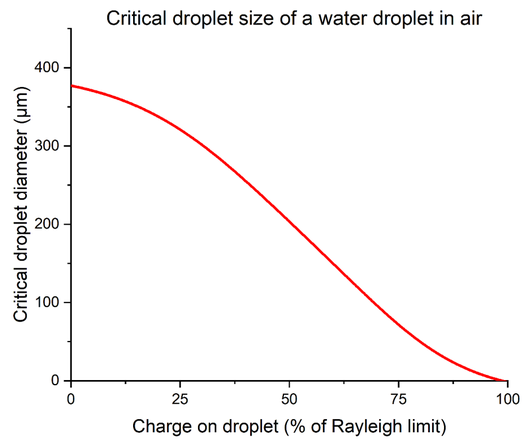
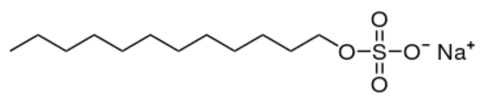


Figure 3. By increasing the amount of charge on the droplets relative to their Rayleigh limit smaller diameters can be ionized.

3. Test the surface selectivity of the instrument

- **It has been demonstrated numerous times that FIDI is surface selective, but it is important to verify this for the smaller droplets being studied here [7, 8]**
- **This could be achieved by varying the ratio of two surfactants that are competing for the surface of the droplet and comparing MS spectra for the droplet bulk and the surface**



Sodium dodecyl sulfate (SDS) – A well studied surfactant that is a strong candidate for testing surface selectivity

4. Perform experiments using the FIDI-MS instrument

Photosensitized reactions of lipids like POPC have been previously studied via FIDI-MS with great success but on much bigger droplets, 2mm. This reaction would be simple to execute and valuable to confirm the oxidation mechanisms on smaller droplets [9]

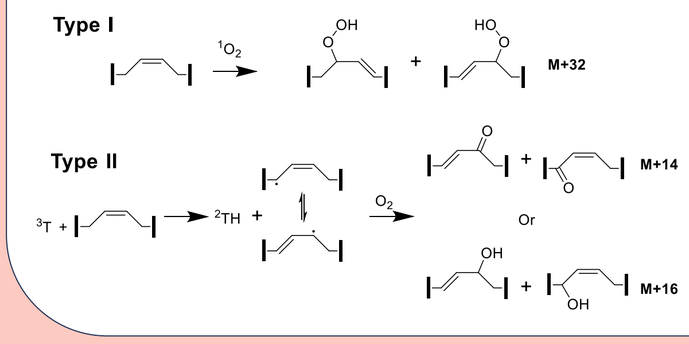


Figure 4. (Left) Photochemical oxidation of POPC with photosensitiser temoporfin

Moving forward the photosensitized reaction of palmitic acid would be a great choice for study due to its atmospheric relevance along with it being unstudied in the droplet environment [5]

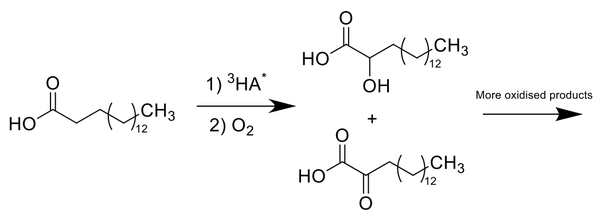


Figure 5. (Above) Photosensitized reaction of palmitic acid in the presence of humic acid

In the future this instrument my have scope to influence a wide range of fields including:

1. **Drug encapsulation – Providing vital information on the composition of the interfaces of droplets containing drug molecules**
2. **Nano particle synthesis – Where droplet surface composition plays a large role in the dried materials shape, structure and composition**
3. **Synthesis chemistry – Where droplets act a micro reactors, accelerating reaction rates (by orders of magnitudes sometimes) compared to macroscopic solutions [4]**

1. B. N. Hendrickson, et al, *Front. Mar. Sci.*, 2021, **7**, 596225
2. R. E. Cochran, et al *Environ. Sci. Technol.*, 2016, **50**, 2477–2486
3. J. Ovadnevaite, et al, Nature, 2017, 546, 637–641
4. B. R. Bzdek, et al, *Commun Chem*, 2020, **3**, 105
5. M. Shrestha, *et al*, Chem. Sci., 2018, 9, 5716–5723
6. O. A. Basaran and L. E. Scriven, Phys. Fluids. A-Fluid, 1989, 1
7. R. L. Grimm and J. L. Beauchamp, J. Phys. Chem. B, 2003, 107
8. R. L. Grimm and J. L. Beauchamp, J. Phys. Chem. B, 2005, **109**
9. C. Mu, *et al*, Angew Chem Int Ed, 2020, 59