A New Approach to Aerosol Thermodynamic and Optical Properties Using Phase Shift Photoacoustic Spectroscopy

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Introduction

- Aerosols **interact with light** directly and indirectly affecting climate radiative forcing [1]
- Direct interactions involve **scattering** and **absorption** and indirect interactions include altering **cloud albedo** by affecting microphysical properties
- Absorption and scattering are quantified by their respective **cross sections**, the sum of these is the **extinction** cross section $\sigma_{ext} = \sigma_{sca} + \sigma_{abs}$
- Aerosol light interactions represent one of the **largest uncertainties** in climate modelling and improvements to measurements are crucial for future improvements[2]
- In particular, the role of **volatile components** in light absorption is not well understood and so this project endeavours to develop a state-of-the-art spectroscopic technique to measure them
- The project will work in collaboration with the Met Office and use **EXSCALABAR**- a suite of cavity ring down and photoacoustic spectrometers which is deployed on the FAAM research aircraft

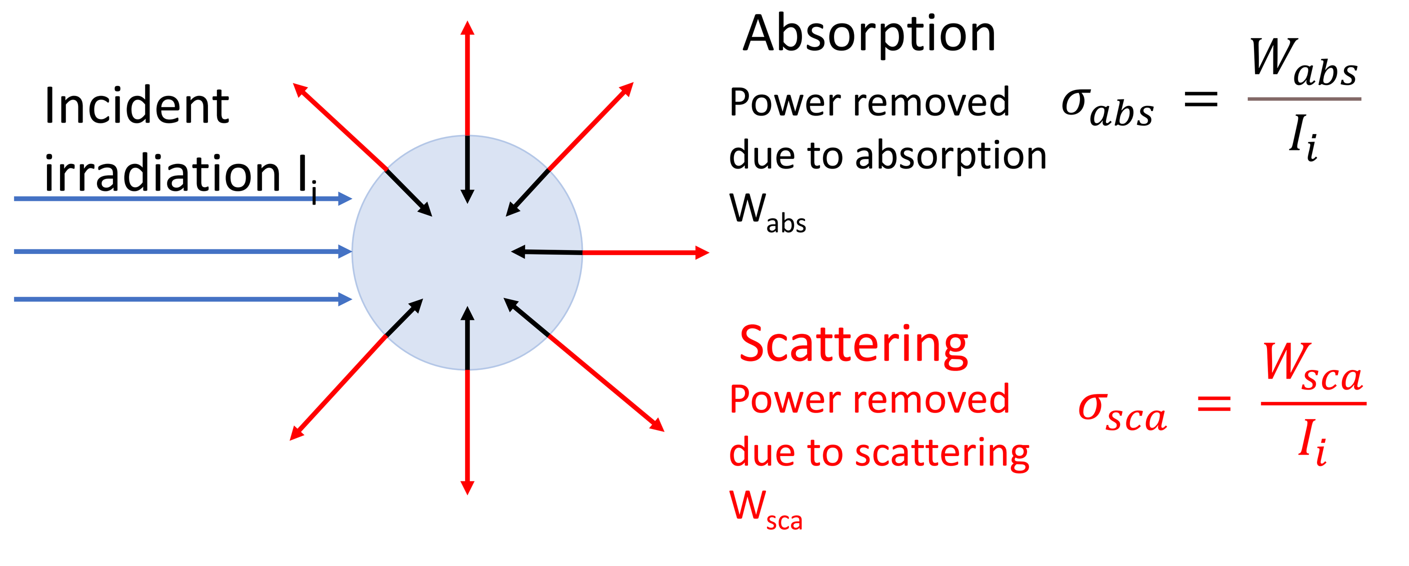

Figure 1: Direct interactions of aerosols with light, the scattering (red) and absorption (black) are represented by their respective cross sections

Cavity Ring-Down Spectroscopy (CRDS)

- Method used to measure the **extinction cross sections** of aerosols [3]
- Laser beam is injected into an optical cavity with two highly reflective mirrors
- The characteristic time of the decay of signal is denoted the **ring-down time**
- Ring-down times for the empty and aerosol laden cavity are recorded
- The extinction cross section is then calculated:

α_{ext} = Extinction coefficient
L = Length of cavity
l = Length occupied by aerosol sample
c = speed of light

$$\alpha_{ext} = \frac{L}{lc}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right)$$

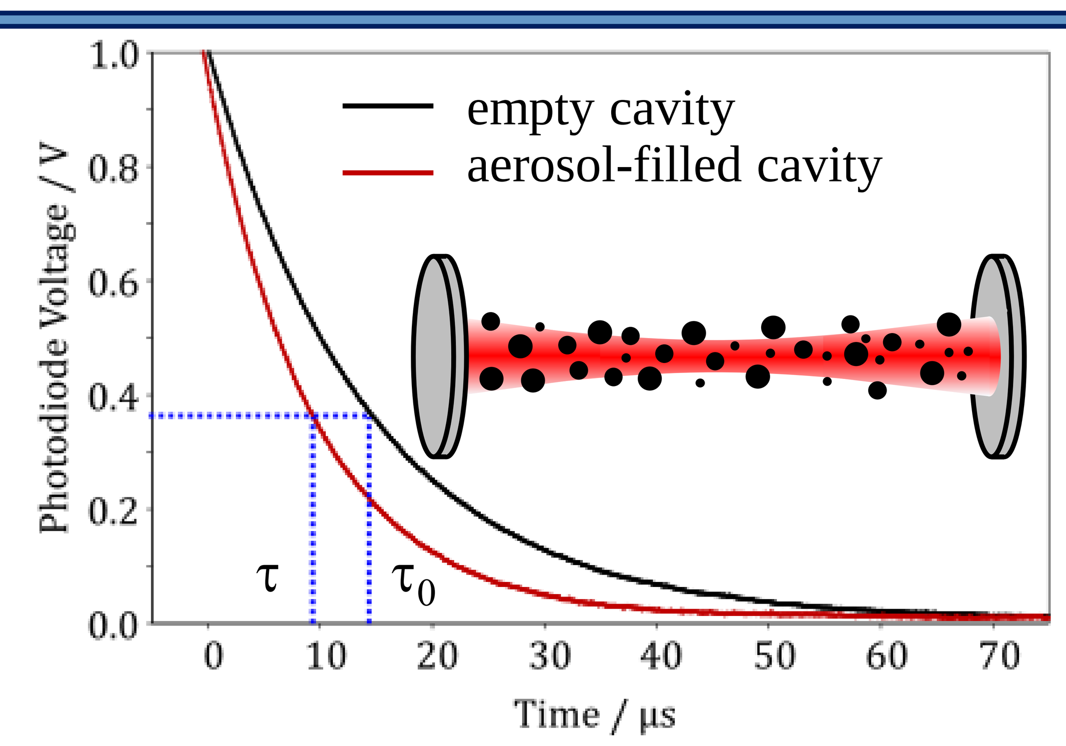

Figure 2: Measurement of ring-down times of an empty and filled cavity in CRDS to determine extinction coefficients

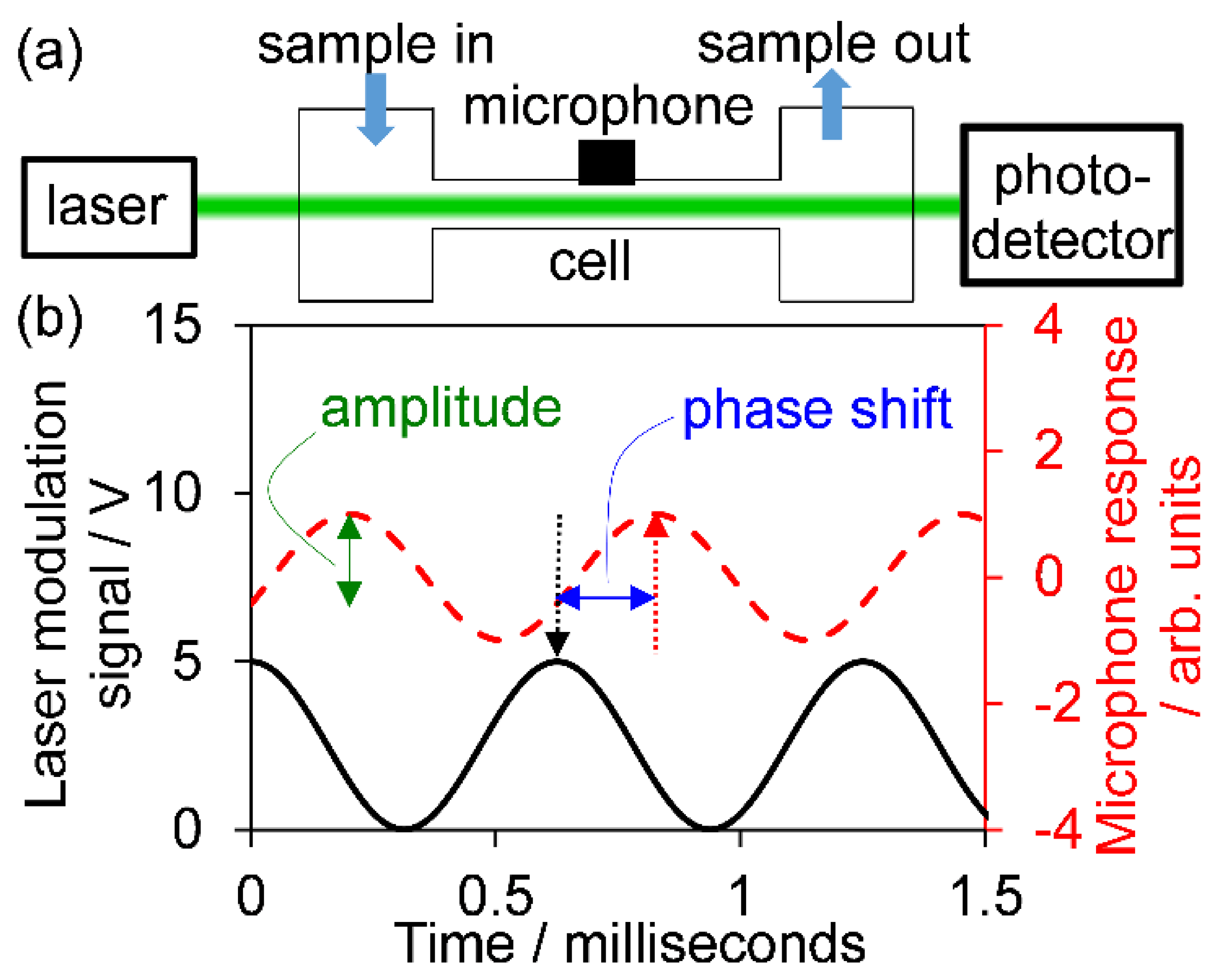

Figure 3: (a) The set-up of photoacoustic spectroscopy to measure the absorption coefficients of aerosol samples which absorb light **(b)** Phase shift in photoacoustic spectroscopy arising from mass flux effects shown by the lag between the modulated laser input (black) and the microphone response (red)

Photoacoustic Spectroscopy (PAS)

- A highly accurate method for determining the **absorption cross-section** [4,5]
- The aerosol sample is irradiated with a periodically modulated laser
- Absorbing aerosols absorb laser light and are **heated**, they then **cool** down by transferring energy to the surrounding bath gas
- The gas molecules undergo **adiabatic expansion** and generate a pressure (sound) wave **detected** by a sensitive microphone
- The amplitude of the response is used to **calculate** the absorption coefficient via a calibration [6]
- Current photoacoustic measurement approaches only allow absorption cross-section measurements for **dry aerosols**, yet atmospheric aerosols often exist as deliquescent droplets

Phase Shift (PS)

- Volatile components have competing **mass flux** pathways which consume energy that would otherwise contribute to the microphone signal [7]
- Initial studies have shown the potential for using the **phase shift**[8], between the periodic modulation of the laser power and the recorded acoustic waveform, that may be recorded to enable light absorption measurements for aerosols containing water or other volatile components such as organics
- It has also been shown that this phase shift can be used to **quantify the volatility** of an aerosol sample

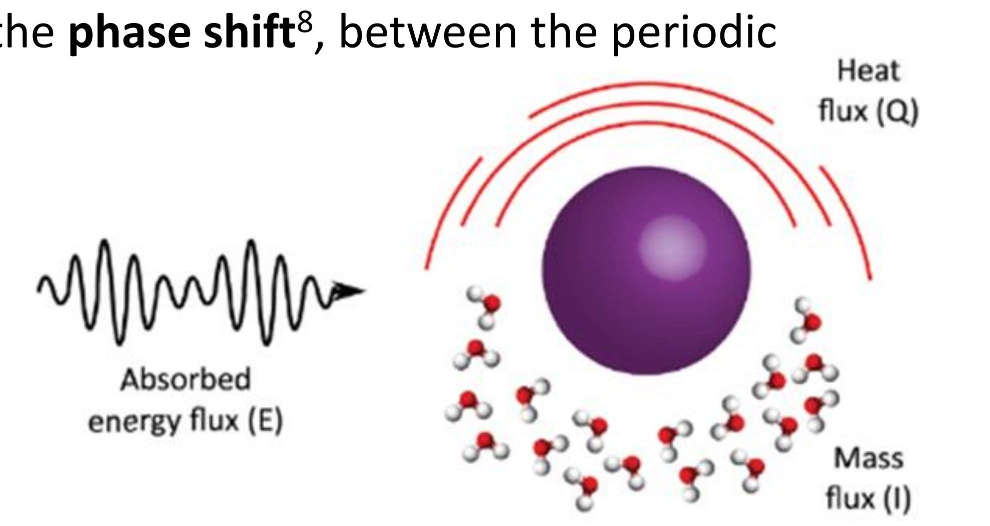

Figure 4: Pathways of energy transfer after an aerosol particle has absorbed light from the incoming modulated laser. Reproduced from Ref. 9

Responsible innovation and policy

- Potential to improve climate models which currently have large uncertainties
- Working in collaboration with the Met Office allows direct benefits to be observed as the instrumentation can be deployed on research aircrafts
- Research will follow UKRI policies, and all work will be published open access
- May support changes in emission policies to limit radiative forcing effects

Challenges

- Developing new technique to be able to access volatile components
- Working to timeframes of access to instruments
- Potential for experimental challenges when accessing high relative humidity, e.g. water vapour may condense on instrumentation affecting measurements

Project Workflow

Using aerodynamic aerosol classifier (AAC) and scanning mobility particle sizer (SMPS) to record mobility size distributions of aerodynamically classified particles

→ Repeat extinction and absorption measurements of Cotterell et al.[10] using an AAC instead of a differential mobility analyser (DMA) to size select particles

→ Using humidifier on EXSCALABAR to investigate optical properties of hydrated particles using the phase shift

→ Extend methodology to use aerosols containing volatile organic compounds

References
1. Ramanathan, V.; Crutzen, P. J.; Kiehl, J. T.; Rosenfeld, D., Aerosols, Climate, and the Hydrological Cycle. *Science* **2001,** *294* (5549), 2119-2124.
2. IPCC, S. f. P. I. C. C. T. P. S. B. C. o.; Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker; T.F., D. Q., G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)].; Cambridge University Press, C., United Kingdom and New York, NY, USA.
3. Mazurenka, M.; Orr-Ewing, A. J.; Peverall, R.; Ritchie, G. A. D., 4 Cavity ring-down and cavity enhanced spectroscopy using diode lasers. *Annual Reports Section "C" (Physical Chemistry)* **2005,** *101* (0), 100-142.
4. Lack, D. A.; Lovejoy, E. R.; Baynard, T.; Pettersson, A.; Ravishankara, A. R., Aerosol Absorption Measurement using Photoacoustic Spectroscopy: Sensitivity, Calibration, and Uncertainty Developments. *Aerosol Science and Technology* **2006,** *40* (9), 697-708.
5. Tian, G.; Moosmüller, H.; Arnott, W. P., Simultaneous Photoacoustic Spectroscopy of Aerosol and Oxygen A-Band Absorption for the Calibration of Aerosol Light Absorption Measurements. *Aerosol Science and Technology* **2009,** *43* (11), 1084-1090.
6. Miklós, A.; Hess, P.; Bozóki, Z., Application of acoustic resonators in photoacoustic trace gas analysis and metrology. *Review of Scientific Instruments* **2001,** *72* (4), 1937-1955.
7. Diveky, M. E.; Roy, S.; David, G.; Cremer, J. W.; Signorell, R., Fundamental investigation of photoacoustic signal generation from single aerosol particles at varying relative humidity. *Photoacoustics* **2020,** *18*, 100170.
8. Cotterell, M. I.; Szpek, K.; Tiddeman, D. A.; Haywood, J. M.; Langridge, J. M., Photoacoustic studies of energy transfer from ozone photoproducts to bath gases following Chappuis band photoexcitation. *Physical Chemistry Chemical Physics* **2021,** *23* (1), 536-553.
9. Diveky, M. E.; Roy, S.; Cremer, J. W.; David, G.; Signorell, R., Assessing relative humidity dependent photoacoustics to retrieve mass accommodation coefficients of single optically trapped aerosol particles. *Physical Chemistry Chemical Physics* **2019,** *21* (9), 4721-4731.
10. Cotterell, M. I.; Szpek, K.; Haywood, J. M.; Langridge, J. M., Sensitivity and accuracy of refractive index retrievals from measured extinction and absorption cross sections for mobility-selected internally mixed light absorbing aerosols. *Aerosol Science and Technology* **2020,** *54* (9), 1034-1057