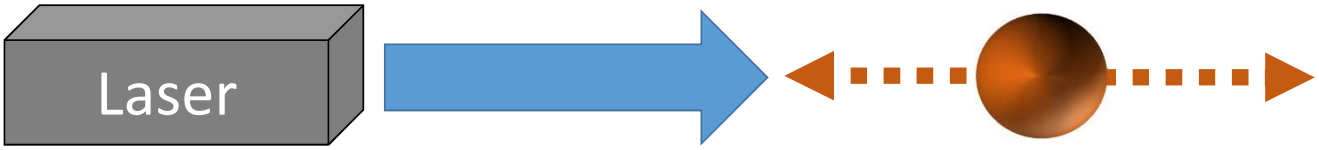
Photophoresis Used for Measurements of Light Absorption by a Single Particle



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how we can use photophoresis for light absorption of aerosols? and what can we gain from that?
Photophoresis is the movement of a particle caused by illumination And an important part of it is a result of light absorption

Motivation: the uncertainty on the effect of aerosols on climate is still high and is partially due to poor constraints on the extent of light absorption by organic aerosols, or BrC.
Main Goal: to be able to perform high sensitivity and high precision measurements of light absorption on a single particle.

in a nutshell

1. Highlights

❖ Photophoresis

Illumination of light absorbing particle generates movement

❖ Used for high sensitivity measurements of the imaginary part of the complex refractive index (κ)

❖ Successful retrieval in the range of $10^{-5} \leq \kappa \leq 10^{-4}$

2. Motivation

❖ Light absorption by atmospheric aerosols is a large source for uncertainty in estimation of effective radiative forcing due to aerosol - radiation interactions.

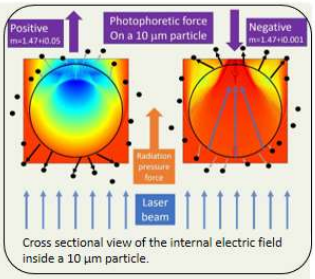
❖ Current measurement techniques suffer from low sensitivity and precision.

3. Methodology

Illuminated, light-absorbing particle experiences a displacing force due to asymmetric heating of its surface.

$F_{ph}(m, a, \lambda, I, K, T, P, \dots)$

$m = n + ik$ complex refractive index
a – particle radius
λ – wavelength
I – radiative flux
K – thermal conductivity
T – initial temperature
P – pressure

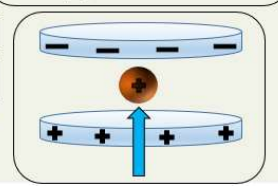


Cross sectional view of the internal electric field inside a 10 μm particle.

$U_{on} \propto (F_g + F_d + F_{ph} + F_{rp})$

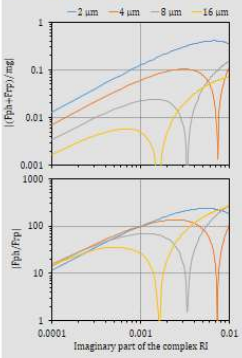
$Laser\ on \rightarrow \frac{\Delta U}{U_{off}} = \frac{F_{ph} + F_{rp}}{F_g + F_d}$

F_g – gravity
F_{ph} – photophoretic force
F_d – drag
F_{rp} – radiation pressure



4. Results

4.1. theoretical



From theoretical consideration:

❖ spherical particles with increasing radii and relatively low values of the imaginary part of the complex refractive index

❖ illuminated with a 20 $mW\ mm^{-2}$ 473 nm laser beam

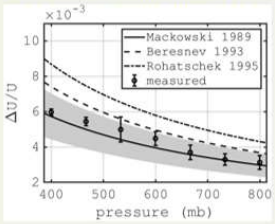
It is shown:

❖ That the sum of optical forces is comparable to the particle's gravity

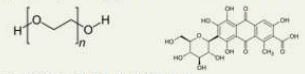
❖ and that F_{ph} dominates over F_{rp}

- Moosmüller, H., Chakrabarty, R.K., Arnott, W.P., 2009, Journal of Quantitative Spectroscopy and Radiative Transfer.
- Steiner, S. S., Krieger, U. K., Te, Y. F., Lienhard, D. M., Huisman, A. J., Luo, B. P., Ammann, M., and Peter, T., 2015, Atmospheric Measurement Techniques.
- Mackowski, D.W., 1989, International Journal of Heat and Mass Transfer.
- Beresnev, S., Chernyak, V., Fomyagin, G., 1993, Physics of Fluids A: Fluid Dynamics.
- Rohatschek, H., 1995, Journal of Aerosol Science.
- Matzler, Christian., 2002. MATLAB functions for Mie scattering and absorption. Institute of Applied Physics.

4.2. measurement – model closure



polyethylene glycol + carminic acid 0.23% wt

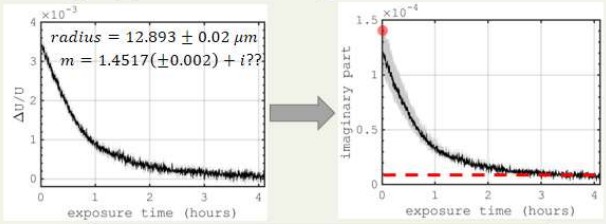


$radius = 9.31 \pm 0.02\ \mu m$

$m = 1.4517(\pm 0.002) + i1.4 \times 10^{-4}(\pm 5 \times 10^{-6})$

Model and measurements agree

4.3. imaginary part retrieval - bleaching



Evolution of light absorption $\kappa \approx 10^{-5}$

5. Conclusion and future work

❖ Closure between measured and calculated optical forces.

❖ Imaginary part retrieval down to $\kappa \approx 10^{-5}$ and $\Delta\kappa < 35\%$

❖ Potential for high sensitivity retrieval of absorption during "browning" and "bleaching" experiments.

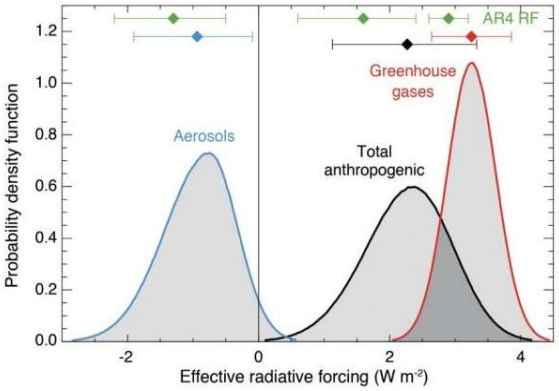
❖ Future developments:

- ❖ Coupling to a soft ionization Electrodynamic Balance – Mass Spectrometer (EDB-MS) for molecular identification of brown carbon evolution
- ❖ Application in a horizontal configuration; decoupling of optical forces and gravity for improved sensitivity.

Why does it matter?

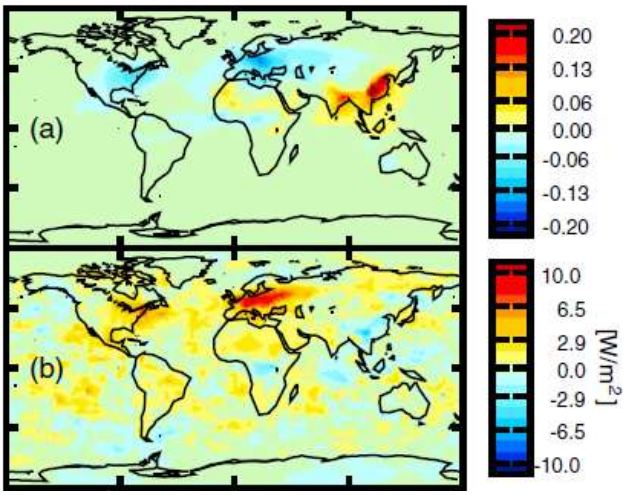
"the Faustian aerosol bargain" (Hansen and Lacis, 1990)

Probability density function of effective radiative forcing

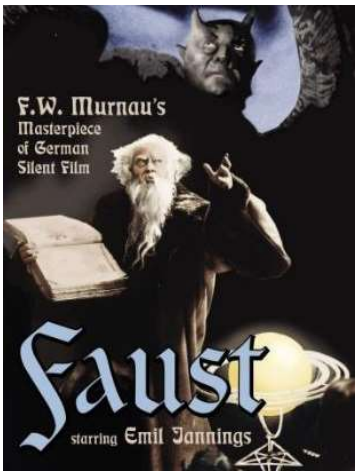


IPCC AR5 WG1 fig 8.16

Simulated change in AOD (a) and ERF (ari and aci) (b) between 1996 and 2010



Kühn et. al. 2014, *Geophys. Res. Lett*



reducing aerosols → warming → how much?

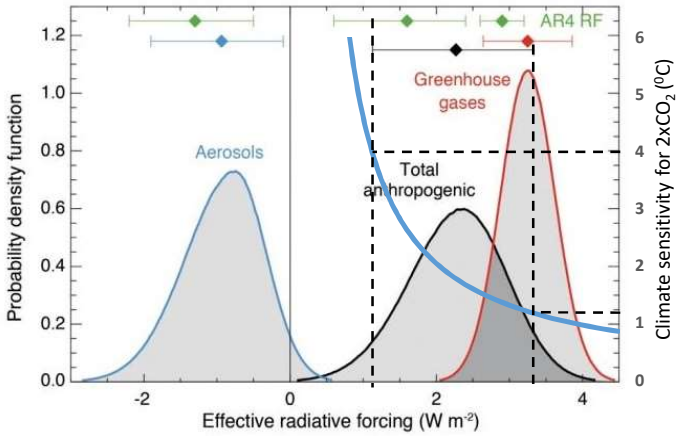
Why should we put effort in studying radiative forcing of aerosols?

Figure on the left describes the estimated RF from aerosols, well mixed green house gases and the total anthropogenic effect. It is clear that aerosols are estimated to have a negative effect, partially masking the warming effect of green house gases. It is also clear that aerosols RF is the largest contributor to uncertainty in total anthropogenic RF. to better understand the climate response to forcing we need to reduce this uncertainty.

Unlike CO2 emission, the geographic distribution of aerosols in the atmosphere is changing very fast.
Middle Figure:
a) simulated change in aerosol loading ->AOD
b) consequent change in RF.
A decrease in aerosol loading over Europe and north America leads to regional warming
An increase over south and south east Asia leads to regional cooling.
This is a result of two processes:
1) inevitable reduction in aerosol emission that is linked to extremely slow phasing out of fossil fuel.
2) the dominant processes is related to emission regulations intended to protect public health from air pollution.
Currently the global average is close to zero but in the future as this trend continues, the cooling effect of aerosols and the related masking of the warming due to GHG will reduce significantly.
Going back to the Figure on the left: This effects is pushing the black curve towards the red one, i.e. accelerating climate warming.
This was referred to as "Faustian bargain": when one thing is sacrificed for another, not necessarily leading to better results. One could apply this here: if within a few decades the masking (cooling) effect of anthropogenic aerosols maybe insignificant. But here lies a problem. We understand that reducing aerosols in the atmosphere leads to warming but how much?

How much warming?

Climate sensitivity



$$transient\ climate\ sensitivity \quad \lambda = \frac{\Delta T}{\Delta F}$$

$\Delta T \approx 1^0 C$ — *global temperature increase since the beginning of the industrial period*

$\Delta F\ [W\ m^{-2}]$ — *total anthropogenic radiative forcing*

$H \approx 0.2\ [W\ m^{-2}]$ — *planetary heat uptake rate (ocean heat uptake)*

$$equalibrium\ climate\ sensitivity \quad \tilde{\lambda} = \frac{\Delta T}{\Delta F - H}$$

$$sensitivity\ to\ doubling\ of\ CO_2 \quad S = \tilde{\lambda} \times F_{2\times CO_2}$$

$$1^0 C \leq S \leq 4^0 C$$

$$IPCC\ AR5\ estimate \quad 1.5^0 C \leq S \leq 4.5^0 C$$

Reducing the uncertainty of aerosols is crucial!!

Climate sensitivity is defined as the globally averaged temperature change in response to changes in radiative forcing.
Transient climate sensitivity does not include slow feedbacks.
To account for these – we introduce the correction factor H which is mostly related to heat uptake by the ocean.
This provides a crud estimate of the climate sensitivity at equilibrium.
We know the current day temperature change relative to pre-industrial period,
So we can use the black curve to plot the range of possible "sensitivity to doubling of the CO2 concentration". A convenient metric that is used to describe the severity of climate change.
The range of uncertainty in total RF leads to a factor of about 4 uncertainty in sensitivity to doubling of CO2.

In blue: the estimated range by IPCC with much more elaborated techniques and models is not very different.
So, reducing the uncertainty in current day RF, which is dominated by aerosols RF is crucial to predict future climate.

Organic Aerosols; “white” or “brown”?

anthropogenic VOC

biogenic VOC

SOA proxies

with/without seed

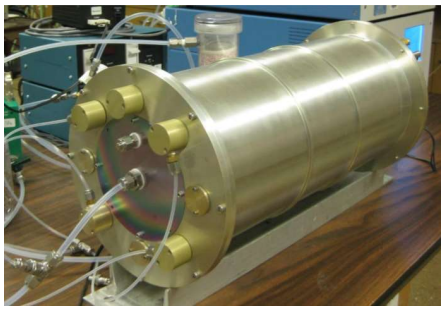
OH oxidation

O_3 oxidation

nitrification

photochemistry

EUROCHAMP2020



Aerodyne research, Inc.

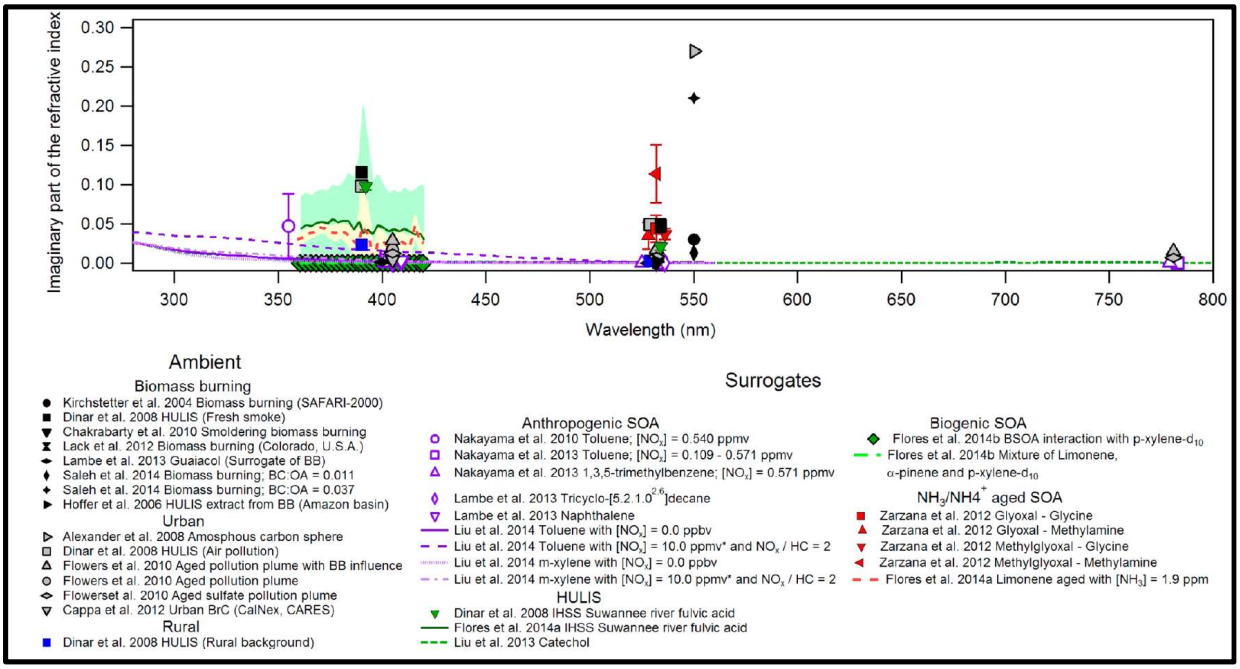
CalTech tube reactor

Organic aerosols are a significate component in the atmosphere, on a local scale they are 20-90% of total aerosol mass
There has been a lot of effort in recent years to better understand how important is light absorption by organic aerosols
and if they absorb light, how does the absorption change with atmospheric aging?

Experiments are done with various precursors such as volatile organic compounds from biogenic or anthropogenic source, different proxies for primary and secondary organic aerosols. With simulating different aging processes and using: Environmental chambers, Reactors, Flow tubes, And in bulk.

Organic Aerosols; “white” or “brown”?

$m = n + i\kappa$ complex refractive index

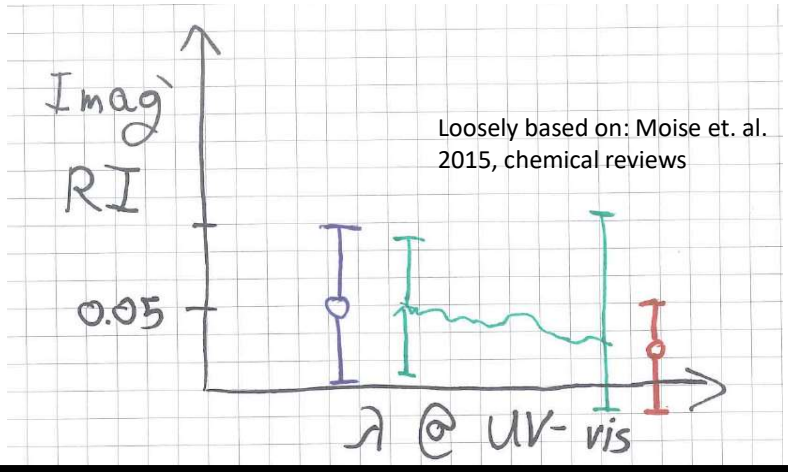


Moise et. al. 2015, chemical reviews

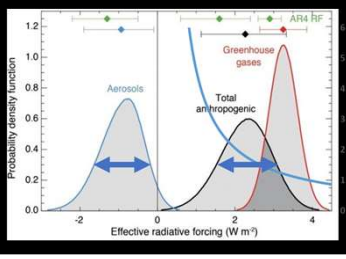
The complex refractive index is an intrinsic optical property of material
Now, because the topic is light absorption, it’s worth remembering that the imaginary part, or the imaginary refractive index describes absorption.
The refractive index is derived, using different methods, from these different types of organic aerosols and atmospheric aging experiments that I mentioned in the previous slide.
This figure, is from a review that was published a few years ago.
There is a lot of information here that we don’t need at the moment but to make a point here I simplified this figure a little bit

Organic Aerosols; “white” or “brown”?

$m = n + i\kappa$ complex refractive index



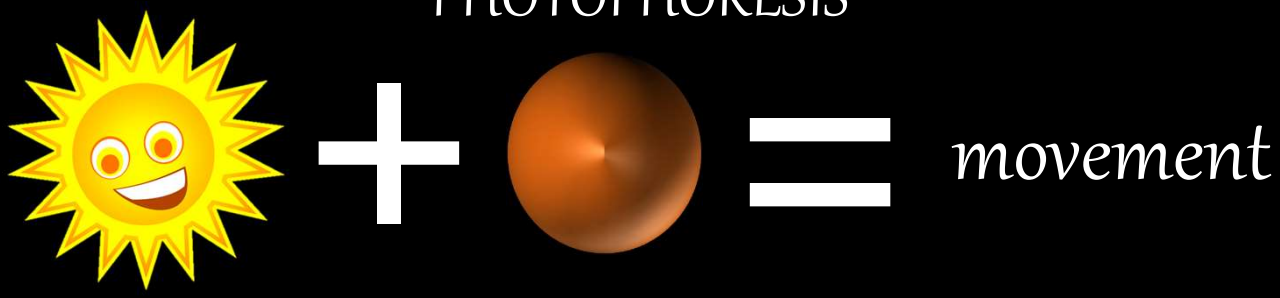
We need to do better!!



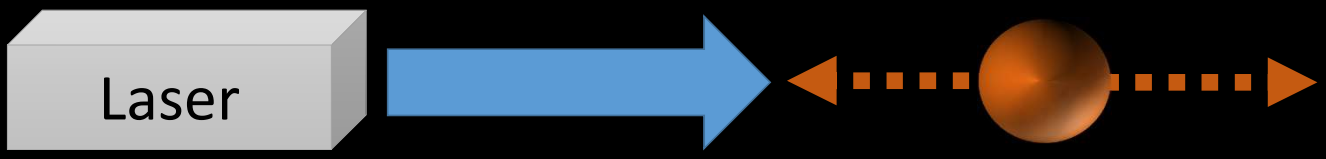
I think that this simplified version of the figure demonstrates the challenge. Each measurement or retrieval method has its advantages and disadvantages BUT the important thing here is that the imaginary part is often reported with **low sensitivity** and **high uncertainty**
sometimes as high as 100% and sometimes more than that, which leads to unphysical results.

We need to improve the uncertainty around radiative forcing of aerosols and this work is about getting higher sensitivity and precision measurements of absorption.

PHOTOPHORESIS



PHOTOPHORETIC - SPECTROSCOPY



Pope et al., 1979; Arnold et al., 1980

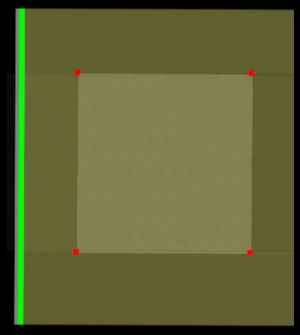
This is how:

Light induces movement in particles, more intensely if they absorb part of this energy.

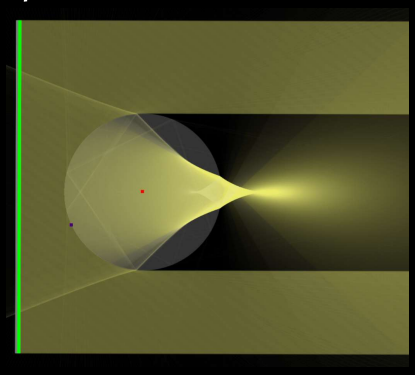
We want to see if we can use this force with photophoretic spectroscopy to quantify the absorption OR the imaginary part of the complex refractive index.

INTERNAL FILEDS

An illuminated glass rectangle

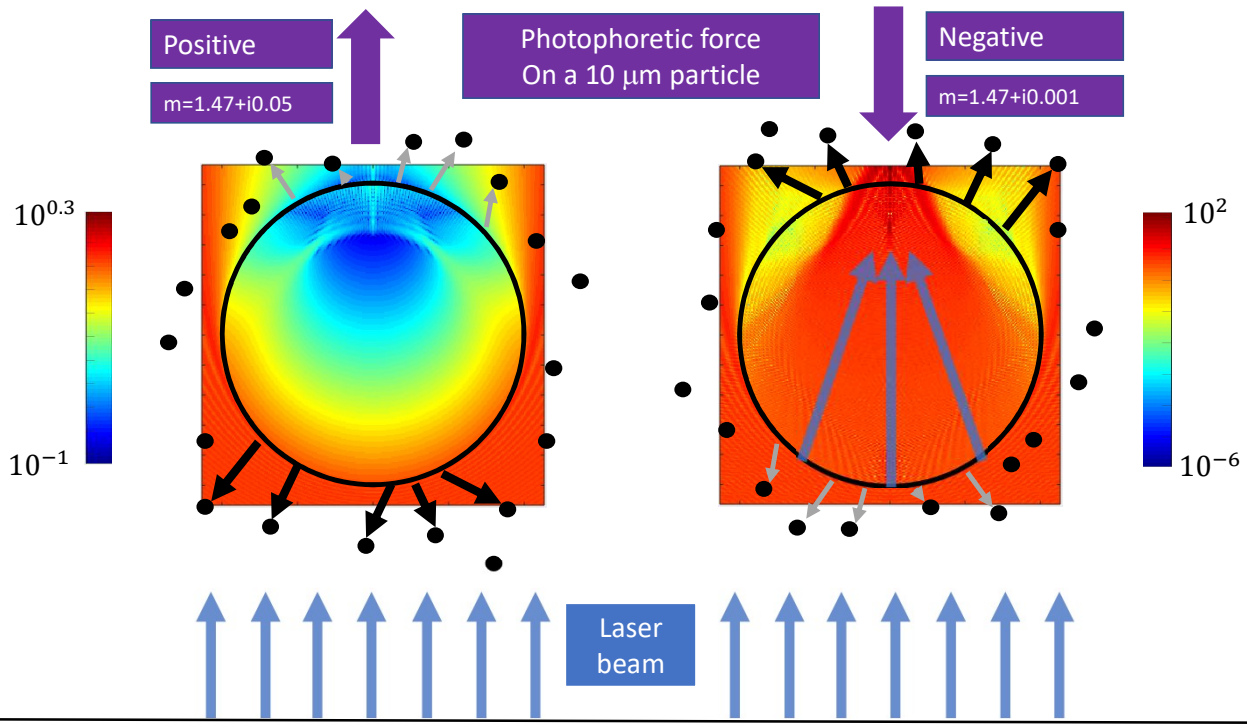


An illuminated glass sphere



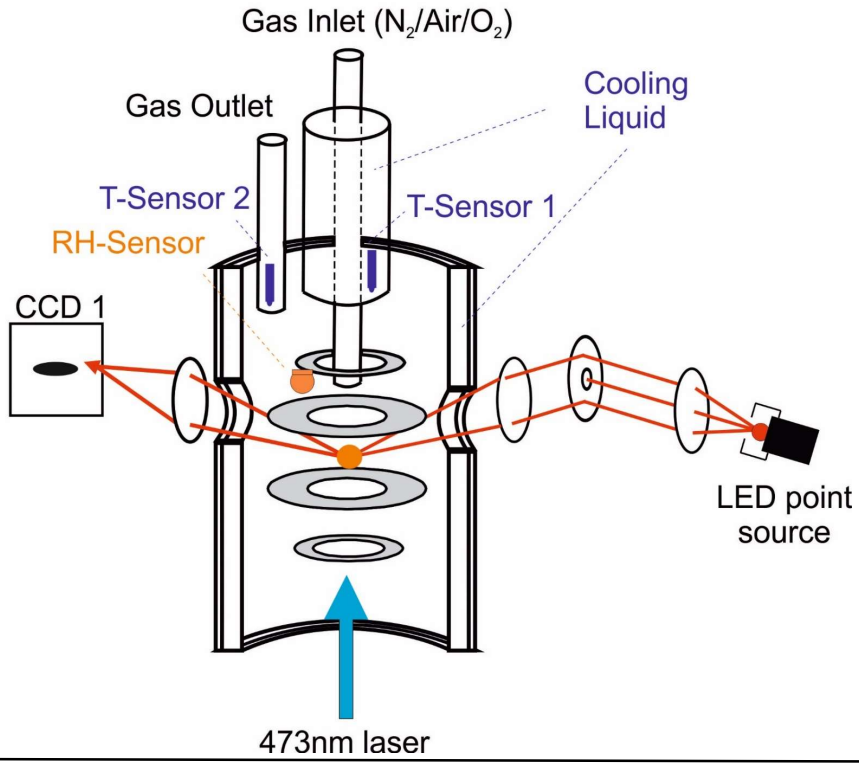
To understand photophoresis and its potential we first need to understand that illuminating a sphere is very different from illuminating a rectangular element like a cuvette for example. Multiple refractions and internal reflections cause a complex structure of the internal electromagnetic fields.

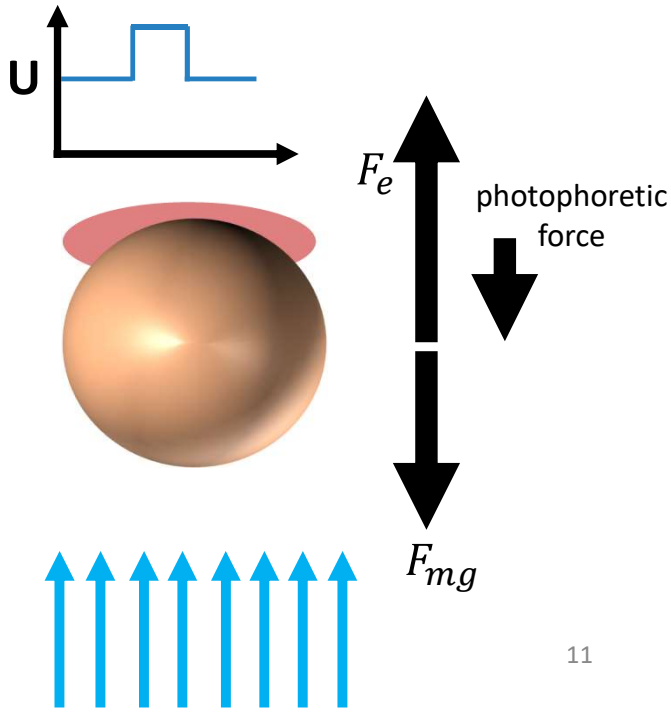
Photophoretic Force on a Levitated Particle



Here are two cross sections of 10 um particles with the same real part of the refractive index (black circle).
The particle on the left has significantly higher absorbing relative to the one on the right.
Both of them are Illuminated from bellow
Inside the particles the color scale is the internal filed intensity relative to the incident beam.
Particle of the left: Most of the energy is absorbed on the illuminated side which is also warmer, and does not propagate through the particle's volume.
Gas molecules around the particle – impact the surface and because the momentum transfer is higher at higher temperature,
The particle is pushed away from the light source, this is called positive photophoresis.
Particle on the right: things get a bit more interesting.
nano-focusing of the energy causes a "hot spot" of intensity on the "dark" side of the particle, and because of absorption also a hot spot of temperature.
as a result the surrounding gas push the particle towards the light source. this is called negative indirect photophoresis
So to calculate the photophoretic force we need to solve the internal field and we also need to know the imaginary part very accurately
Inversely, if we measure the force we can retrieve the imaginary part

Electrodynamic Balance (EDB) setup

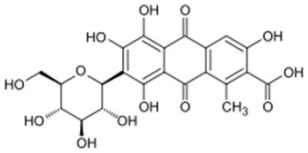


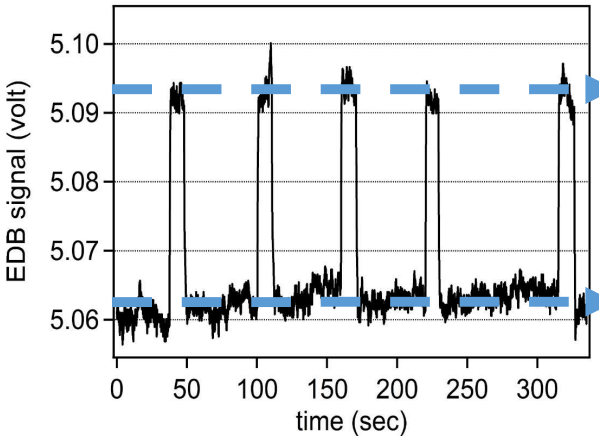


In our experimental set-up we use the electrodynamic balance, or EDB to trap a charged particle in an electric field, generated by 4 electrodes (gray rings).
The balance is very sensitive to fluctuations in the vertical force that is acting on the particle.
its is housed in a chamber that we can use to control the environment (temperature, RH, pressure, gas)
So we can imitate realistic atmospheric conditions around the particle
We use a camera to track the position of the particle and change the voltage to move it back to the center in case its trying to move away.
In the baseline condition the voltage is proportional to (mostly) gravity.
When we turn the laser on, the “dark” side of the particle gets warmer and the photophoretic force pulls the particle down. As a result the voltage increases to compensate.
When we turn the laser off and the signal return to baseline.

ElectroDynamic Balance (EDB) setup

polyethylene glycol + carminic acid

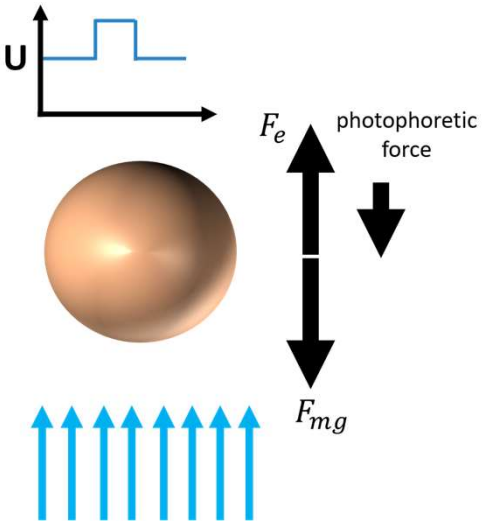




$U_{on} \propto gravity + drag + photophoresis$

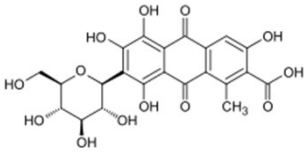
$U_{off} \propto gravity + drag$

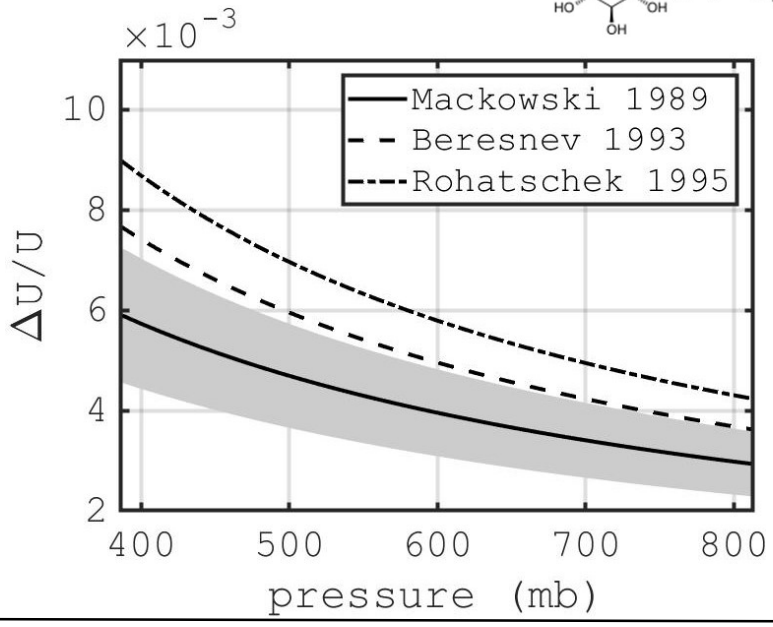
$$\frac{\Delta U}{U_{off}} = \frac{photophoresis}{gracity + drag}$$



ElectroDynamic Balance (EDB) setup

polyethylene glycol + carminic acid





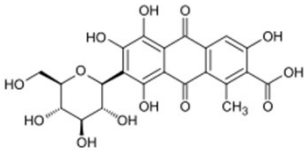
$$\frac{\Delta U}{U_{off}} = \frac{photophoresis}{gracity + drag}$$

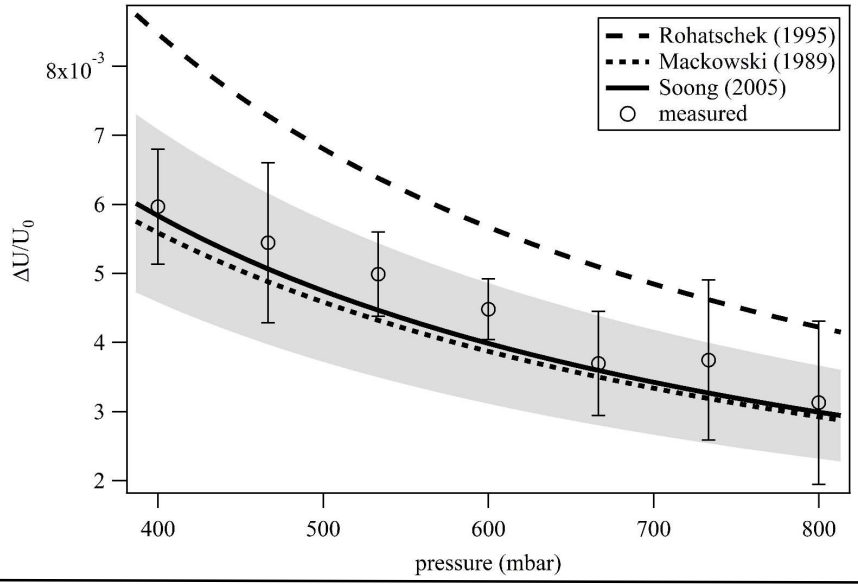
with using available models of the photophoretic effect and calculation of the internal filed we can model the experimental system

For convenience I show uncertainties only on one of the models but its almost identical for all of them

ElectroDynamic Balance (EDB) setup

polyethylene glycol + carminic acid





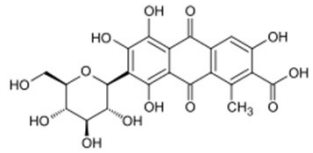
$$\frac{\Delta U}{U_{off}} = \frac{photophoresis}{gracity + drag}$$

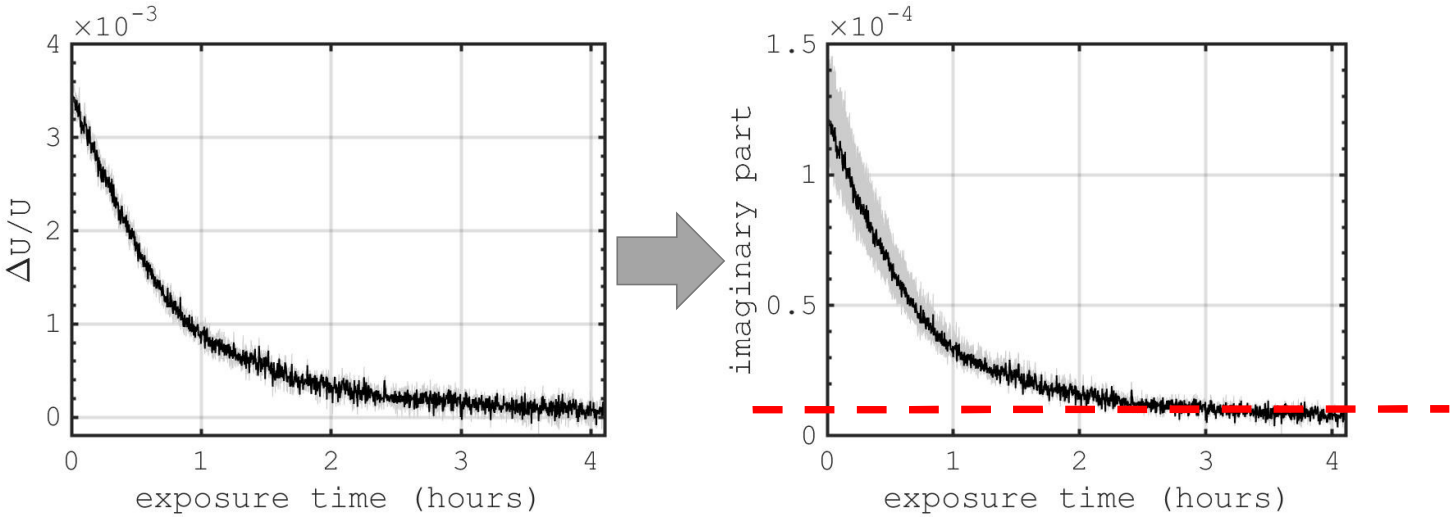
Model and measurements agree

When we add the measurements to the plot its clear that we have agreement with the model and we can use it to retrieve absorption of an ‘unknown’ particle

Results: photolysis and absorption decay

polyethylene glycol + carminic acid





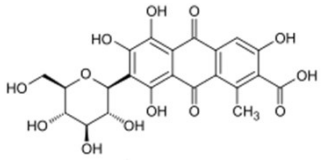
Evolution of light absorption $\kappa \approx 10^{-5}$

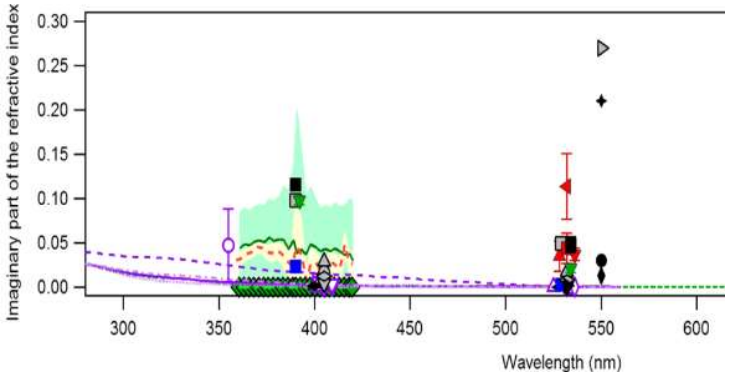
It just so happens that carminic acid photolyase with exposure so we can follow the decay in absorption.
This a nice example for a BrC ‘bleaching’ (proxy) experiment – to see how the absorption evolve with aging.
It’s the same chemical system as before but a different particle.

Here we use the model to retrieve the imaginary refractive index and one can imagine that we can use the same approach to follow ‘browning’ experiments.
Realistically with this setup the sensitivity we can get from this system is about 10^-5

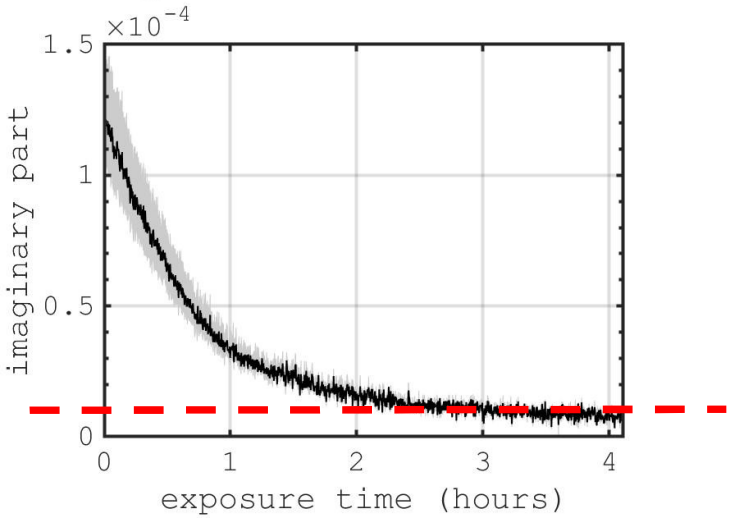
Results: photolysis and absorption decay

polyethylene glycol + carminic acid





Moise et. al. 2015, chemical reviews

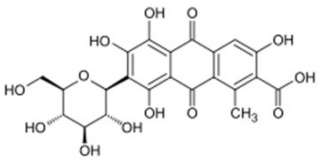


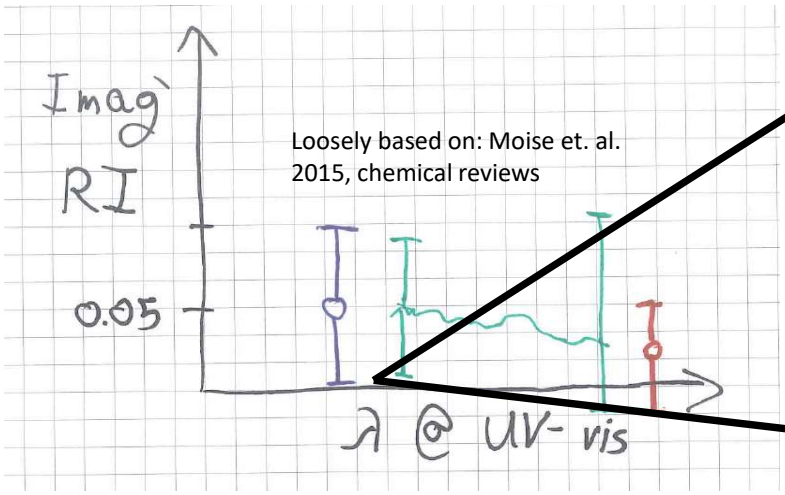
Evolution of light absorption $\kappa \approx 10^{-5}$

A quick remainder of the figure I showed before.

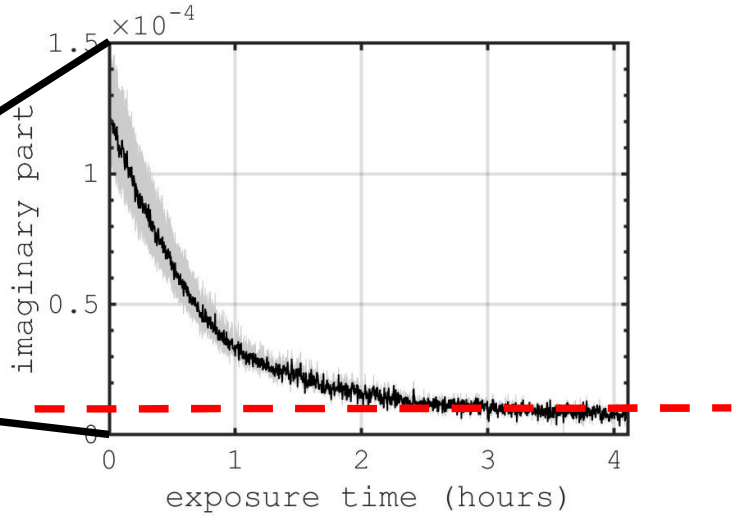
Results: photolysis and absorption decay

polyethylene glycol + carminic acid





Loosely based on: Moise et. al. 2015, chemical reviews



Evolution of light absorption $\kappa \approx 10^{-5}$

Or the simplified version

We can use photophoretic spectroscopy to resolve absorption that other particle-phase techniques struggle with

Publication: currently AMT discussion

Submitted as: research article 04 Mar 2020

Review status
This preprint is currently under review for the journal AMT.

Photophoretic spectroscopy in atmospheric chemistry – high sensitivity measurements of light absorption by a single particle

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Abstract. Light absorbing organic atmospheric particles, termed brown carbon, undergo chemical and photochemical aging processes during their lifetime in the atmosphere. The role these particles play in the global radiative balance and in the climate system is still uncertain. To better quantify their radiative forcing due to aerosol-radiation interactions, we need to improve process level understanding of aging processes, which lead to either "browning" or "bleaching" of organic aerosols. Currently available laboratory techniques aim to simulate atmospheric aerosol aging and measure the evolving light absorption, but suffer from low sensitivity and precision. This study describes the use of electrodynamic balance photophoretic spectroscopy (EDB-PPS) for high sensitivity and high precision measurements of light absorption by a single particle. We demonstrate the retrieval of time-evolving imaginary part of the refractive index for a single levitated particle in the range of 10^{-4} to 10^{-5} with uncertainties of less than 25 % and 60 %, respectively. The experimental system is housed within an environmental chamber, in which aging processes can be simulated in realistic atmospheric conditions and lifetime of days to weeks. This high level of sensitivity enables future studies to explore the major processes responsible for formation and degradation of brown carbon aerosols.

How to cite: Bluvshtein, N., Krieger, U. K., and Peter, T.: Photophoretic spectroscopy in atmospheric chemistry – high sensitivity measurements of light absorption by a single particle, Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2020-68, in review, 2020.

IAC Institute for Atmospheric and Climate Science

‘browning’ of sulfuric acid particle

Aldol condensation reaction ??

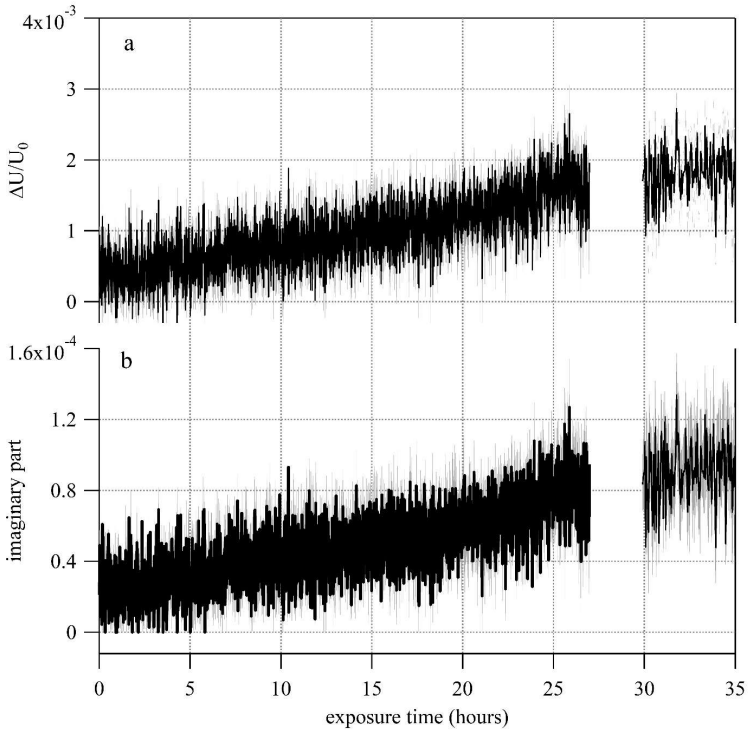
H_2SO_4 droplet at ‘dry’ conditions

≈82.3% wt (Krieger et al 2000 applied optics)

0 ^{0}C and 400 mbar

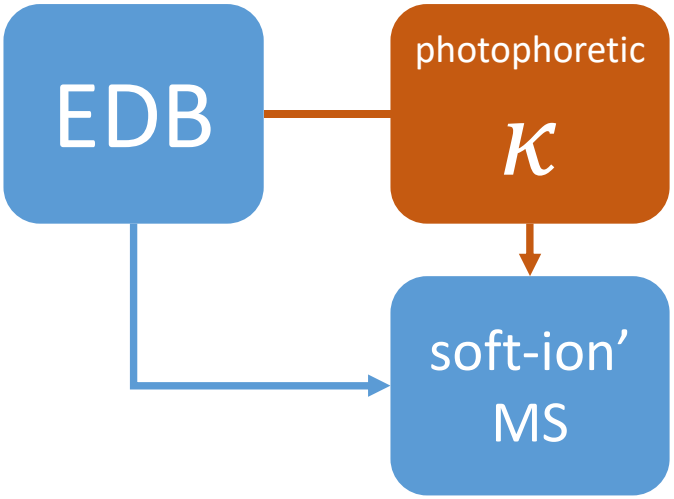
Dp ≈ 16 µm

Formaldehyde max conc’ ≈ 300 ppb



Preliminary results of application to ‘browning’ of sulfuric acid droplet exposed to organic vapor.

Future developments

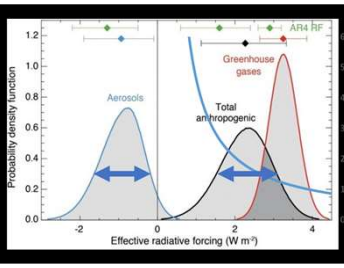



Ulrich Krieger


me


Marcel Muller

Evolution of light absorption AND of molecular species



Where do we want to go with photophoretic spectroscopy in the future?

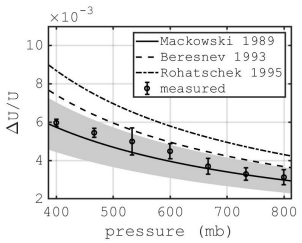
A PhD student in our group is now working on developing the EDB soft-ionization MS which will allow molecular level characterization of atmospheric aging processes

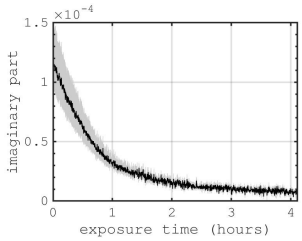
What I intend to do is to introduce the PPS in to that system and to link absorption to chemical species as both evolve under real world conditions

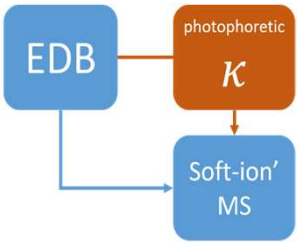
Hoping that we can contribute to reducing uncertainty on the radiative forcing of aerosols

Conclusions

- Agreement between measurements and model (Mackowski 1989)
- High sensitivity retrieval of the imaginary part of the complex refractive index ($\approx 10^{-5}$)
- Potential contribution: fate of light absorbing compounds
- Future development: coupling with soft ionization mass spectroscopy – identification of chromophores





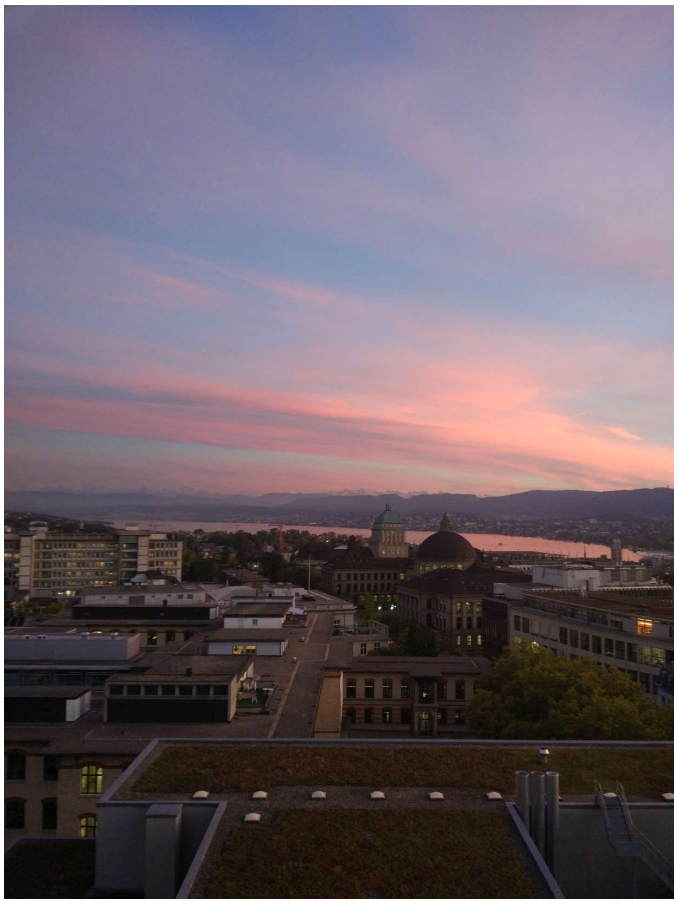


Acknowledgments

- ETH postdoctoral fellowship program

See here:

- Mentors – Atmospheric Chemistry Group
  - Prof' Thomas Peter
  - Dr. Ulrich Krieger



Conclusions

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- ❖High sensitivity retrieval of the imaginary part of the complex refractive index ($\approx 10^{-5}$)
- ❖Potential contribution: fate of light absorbing compounds
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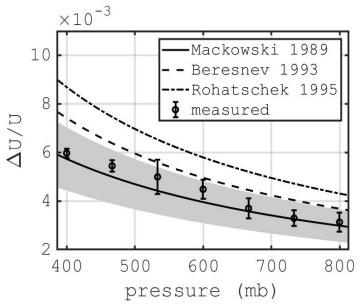

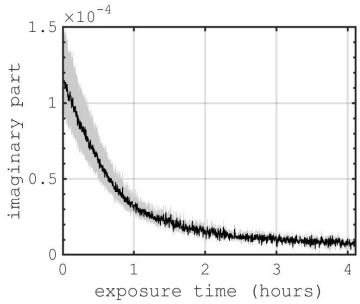

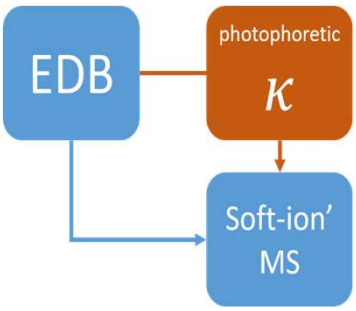

For more information (on this topic and on the group: