Atmos. Meas. Tech. Discuss.,
doi:10.5194/amt-2020-68-AC1, 2020

Atmospheric Measurement Techniques
Discussions

Interactive comment on “Photophoretic spectroscopy in atmospheric chemistry – high sensitivity measurements of light absorption by a single particle” *by* Nir Bluvshtein et al.

Nir Bluvshtein et al.

nir.bluvshtein@env.ethz.ch

Received and published: 15 April 2020

We would like to thank Anonymous Referee #1 for carefully reading our submitted manuscript and for raising important and insightful questions that helped us improve the quality and readability of the manuscript.

answer to question #1:

There are no theoretical upper and lower limits for retrievals of κ using the described method. On the lower end, this would depend on the sensitivity and stability of the experimental set-up. With our system, which could be improved, as mentioned in the

manuscript this value is about 10ˆ-5. On the upper end of κ values, more energy is absorbed and as a result, the signal is generally (not always, see below) stronger and easier to measure. However, this should be compensated with reducing the power of the light source to avoid significant temperature change of the particle.

We chose to emphasize the usefulness of EDB-PPS at the lower range of κ. Because at higher values of κ, other particle-phase techniques are available, that are simpler to implement. These include photoacoustic spectroscopy, cavity-enhanced spectroscopy, extinction minus scattering, and filter based techniques. Therefore one can expect this method to be mostly rewarding at $\kappa \leq$ 10ˆ-3 in aging experiments that are intended to follow ‘bleaching’ or ‘browning’ of BrC.

To better explain the limitations of this technique with regards to a useful range of the imaginary part we added the following figure (figure 1 below). This figure illustrates the simulated system signal (ΔU/U0) over 6 orders of magnitude of κ, from 10ˆ-8 to 10ˆ-2, of a 10 μm, PEG400 based particle. At the lower end of this range (left side of figure 1a), κ is effectivity zero and the simulated signal is negative (particle moves away from the light source) due to direct photophoresis (radiation pressure) alone. Note how the signal increases to positive values as κ increases (figure 1a and 1b) due to an increase in the thermal asymmetry parameter. With the increase in κ there more energy that is absorbed on the illuminated side of the particle. This offsets the hotspot of absorbed energy at the ‘dark’ side of the particle that is due to ‘nano-focusing’. As a result, the thermal asymmetry parameter is reduced together with the signal. As κ continues to increase the asymmetry parameter changes sign from positive to negative as the illuminated side of the particle becomes warmer than the ‘dark’ side. This is shown in figure 1c as a negative signal and illustrated in 1d as the particle shifts from the regime described by the upper part to the one in the lower part of figure 1d.

Based on this description and on our system’s sensitivity limitations we determined the lower limit for κ retrieval at 10ˆ-5 and do not determine an upper limit. We do, however, note areas with high uncertainty, namely, around $\kappa \approx$ 10ˆ-3, where the change in signal flattens.

An important caveat is a non-injective behavior in figure 1b. To address the issue one would need to understand the order of magnitude of the particle's absorption (for example; is it below or above κ = 10ˆ-3). Additionally, in aging experiments, as κ evolves, the direction of the change of the signal would clarify the direction of the change of κ.

This figure will be added as figure #7 and a descriptive text will be added to the conclusion section in the revised version of this manuscript to describe the figure and the simulated system behavior in different absorptivity regimes.

answer to question #2:

The retrieved refractive index or the imaginary part of the refractive index, like in other retrieval methods, is that which best represent the optical properties of the measured particle. For a single composite particle that would be the refractive index of the bulk material. For a multi-component particle (miscible liquids, solutions, etc.) the retrieved refractive index sometimes referred to as an effective refractive index could be different from that of the individual materials. In the results given in this manuscript, the retrieved imaginary part is not that of carminic acid and not that of PEG400. It is the imaginary part of the specific mixture and is a product of the amount of light absorbed by the particle. A different type of absorbing molecules i.e. with higher or lower molar absorptivity at higher or lower concentration would yield a different imaginary part based on the amount of light absorbed by the mixture. In this respect, this method is not different from any other retrieval method in bulk, thin film or in the particle phase.

answer to question #3:

Illuminating light-absorbing particles results in inevitable temperature change that is related to the amount of light absorbed and to the materials heat capacity. For the particles in this study, the temperature change is estimated to be below 1 K by using

the heat conductivity equation (from 0.02 to 0.4 K, depending on κ and on the size of the particle). In equilibrium, this would also depend on the heat conductivity of the particle and its surrounding and the surrounding temperature. A hydrated particle, upon increasing temperature, will lose some water and will reach a new equilibrium with its environment at lower water activity even though the RH remains unchanged. This also means that at equilibrium the particle will be smaller. The extent of this effect depends on the temperature change within the particle. This effect was used as a method to retrieve κ (Knox & Reid, 2008; Willoughby et al., 2017). There is no theoretical limitation for retrieval of κ using EDB-PPS at elevated RH conditions. Temperature equilibrium is reached within milliseconds while water activity and size equilibrium are reached depending on the particle diffusivity. In the case of PEG400, this happens within a time scale of about 1 second. As long as equilibrium is reached, the signal can be used. The added complexity compared to a dry experiment is that parameters such as thermal conductivity of the particle and of the environment as well as the size of the particle (before and during illumination) are needed. We have performed several experiments with the PEG400-CA system at elevated RH. In these experiments, the size of the particle before illumination is retrieved with the high resolution scattering spectra as described in the manuscript, while the instantaneous size change due to water lose/gain was monitored with using low resolution scattering spectra at 1 Hz at a resolution of about 1 nm (Steimer et al., 2015). It was clear that size (and water activity) equilibrium was reached within 1 second/spectrum. Further exploring this application was beyond the scope of this manuscript but will most likely be a part of future implementation of the EDB-PPS.

Knox, K. J., & Reid, J. P. (2008). Ultrasensitive absorption spectroscopy of optically-trapped aerosol droplets. Journal of Physical Chemistry A, 112(42), 10439–10441. https://doi.org/10.1021/jp807418g

Steimer, S. S., Krieger, U. K., Te, Y. F., Lienhard, D. M., Huisman, A. J., Luo, B. P., Ammann, M., & Peter, T. (2015). Electrodynamic balance measurements of thermodynamic, kinetic, and optical aerosol properties inaccessible to bulk methods. Atmos. Meas. Tech., 8(6), 2397–2408. https://doi.org/10.5194/amt-8-2397-2015

Willoughby, R. E., Cotterell, M. I., Lin, H., Orr-Ewing, A. J., & Reid, J. P. (2017). Measurements of the Imaginary Component of the Refractive Index of Weakly Absorbing Single Aerosol Particles. Journal of Physical Chemistry A, 121(30), 5700–5710. https://doi.org/10.1021/acs.jpca.7b05418

answer to question #4:

This technique does not require the sample to be dissolved in PEG400 or any other solvent. The goal of this work is to retrieve low levels of κ; in a range, other particle-phase techniques are not sensitive enough. For this reason, PEG400 was used as a non-absorbing organic matrix that allows for the total absorptivity of the particle to be much lower compared to pure carminic acid. Nevertheless, as the reviewer pointed out, a disadvantage of this method is the need for some parameters to be well characterized. Amongst others, these include thermal conductivity (of both particle and gas phase) and thermal accommodation coefficient.

Thermal conductivity: uncertainty in thermal conductivity leads to uncertainty in the retrieved κ. As an example, an uncertainty of 30% in the thermal conductivity leads to a non-symmetric 20 – 30% uncertainty in retrieved κ in the range of 10-5 – 10-3. The range of uncertainty is due to the non-linearity of κ with ΔU/U0.

One way to reduce the uncertainty is to perform measurements of an unknown absorbing material which is highly diluted or well mixed with a well-characterized material (such as PEG400, water, sulfuric acid). In this way, the thermal properties of the particle are assumed identical to the thermal properties of the well-characterized material.

An additional approach for unknown, atmospherically relevant organic material is to consider that many organic compounds are very similar with respect to their thermal properties and use an approximated value with an appropriate uncertainty. We refer the

reviewer to the literature survey by Latini et al (2014) that compiled thermal conductivity data for the following 3400 data sets (excluding additional 1340 data sets of refrigerant compounds) at atmospheric pressure and reduced temperature of about 0.6 ± 0.14.

Thermal accommodation coefficient (αT): the literature on measurements or estimations of αT is scarce. As a result, one must simply assume a reasonable value. It is important to note that an error in αT propagates to relatively small errors in the retrieved κ. For example, the value that we used in this study i.e. αT=0.85 ±0.15 ($\pm\sim$18%) leads to a non-symmetric 5 – 7% uncertainty in retrieved κ in the range of 10ˆ-5 – 10ˆ-3.

This discussion will be added to the last paragraph in section 3 of the revised manuscript.

Latini, G., Di Nicola, G., & Pierantozzi, M. (2014). A critical survey of thermal conductivity literature data for organic compounds at atmospheric pressure and an equation for aromatic compounds. Energy Procedia, 45, 616–625. https://doi.org/10.1016/j.egypro.2014.01.066

answer to question #5:

For non-absorbing particles, the only effect from illuminating it would be that of the direct photophoresis (radiation pressure), which is about 1 – 2 orders of magnitude smaller than indirect photophoresis in our experimental range. Its direction is always away from the light source so if detectable, it should result in a negative signal (i.e. negative ΔU/U0).

An experiment with undyed PEG400 particle showed no detectable signal (i.e. above noise level). The following text will be added to section 3: “It is important to note that as expected, for a pure PEG400 particle (i.e. no measurable absorption at 473 nm) at similar conditions, but a slightly less sensitive setup, no signal could be detected.”

answer to question #6:

We agree with the reviewer and mentioned this in the text, that a significant disadvantage of bulk and film type of experiments is that supersaturated conditions are not accessible.

This point will be made clearer at the end of the introduction section of the revised version of the manuscript.

answer to question #7:

If the reviewer is referring to figure 3, this figure shows the resonance peaks which are labeled on the theoretical curves and additional noise oscillations that extend the full spectra in both polarizations. These oscillations are caused mainly by variations in the laser power as the length of its optical cavity is changing. The particle horizontal movement due to the AC field sometimes causes an additional noise component. Most (but not all) of the first component is reduced by dividing the particle spectrum by a reference spectrum. Note that in this study, the particle was not illuminated with the "heating" beam while scanned with the TDL laser.

The following text will be added to the figure caption: "Residual noise in the measured spectrum originates mostly from laser power oscillations due to frequency scanning operation and from the horizontal oscillation of the particle due to the applied AC field."

answer to question #8:

The following figure 2 will be added to the revised manuscript.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2020-68, 2020.

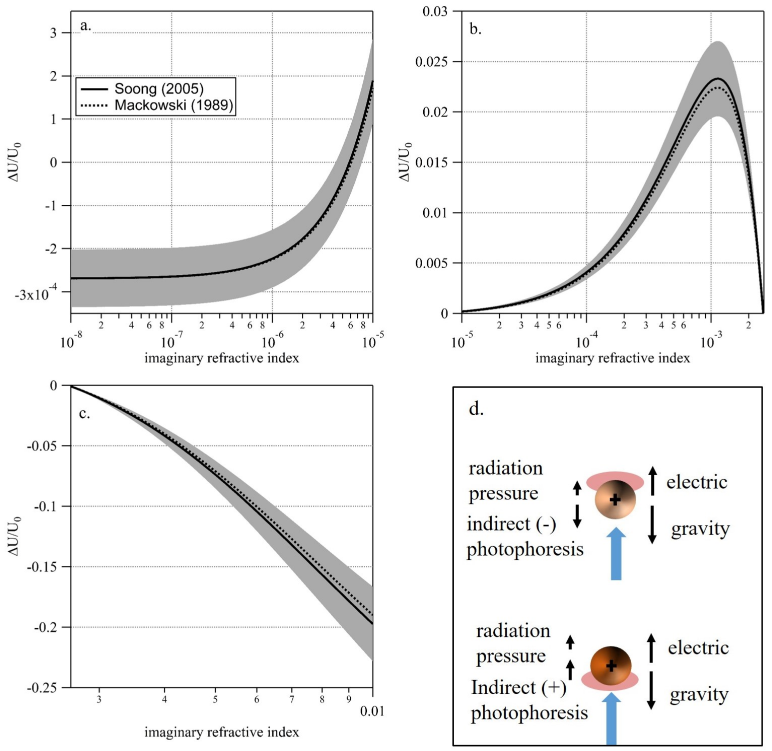

Fig. 1. simulated signal (and uncertainty) for a PEG400 particle, 10 μm in radius at T = 20 C, P = 400 mbar, m1=1.466, λ=473 nm, I=35 mW mmˆ-2 and full thermal accommodation.

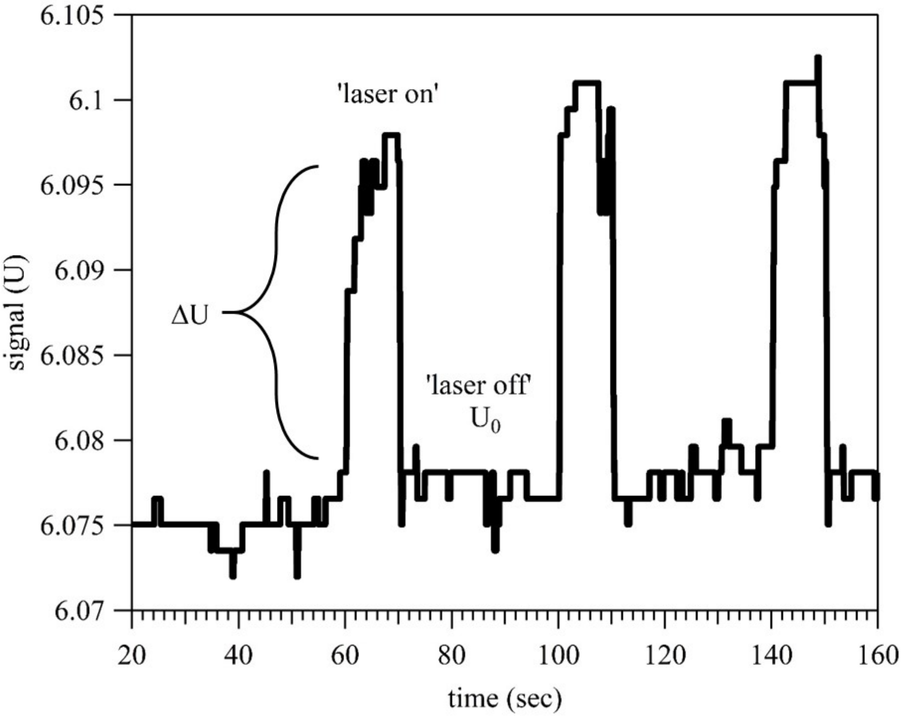

Fig. 2. change in the applied DC voltage in response to alternately illuminating a trapped light absorbing particle. Here, a particle with 12.72 μm radius and $\kappa \approx 1.36 \times 10$ˆ-4.