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Conference Paper**Author(s):**

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Publication date:

2017

Permanent link:

<https://doi.org/10.3929/ethz-b-000234676>

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Originally published in:

10347, <https://doi.org/10.1117/12.2275627>

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Paul A. Covert, Johannes W. Cremer, Ruth Signorell, "Photoacoustic absorption spectroscopy of single optically trapped aerosol droplets," Proc. SPIE 10347, Optical Trapping and Optical Micromanipulation XIV, 1034729 (25 August 2017); doi: 10.1117/12.2275627

SPIE.

Event: SPIE Nanoscience + Engineering, 2017, San Diego, California, United States

Photoacoustic absorption spectroscopy of single optically trapped aerosol droplets

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ABSTRACT

Photoacoustics have been widely used for the study of aerosol optical properties. To date, these studies have been performed on particle ensembles, with minimal ability to control for particle size. Here, we present our single-particle photoacoustic spectrometer. The sensitivity and stability of the instrument is discussed, along with results from two experiments that illustrate the unique capabilities of this instrument. In the first experiment, we present a measurement of the particle size-dependence of the photoacoustic response. Our results confirm previous models of aerosol photoacoustics that had yet to be experimentally tested. The second set of results reveals a size-dependence of photochemical processes within aerosols that results from the nanofocusing of light within individual droplets.

Keywords: counter-propagating tweezers, trapping stability, thermal inertia, nanofocusing, photokinetics

1. INTRODUCTION

The photoacoustic (PA) effect describes the conversion of modulated light energy into acoustic energy through rapid thermal fluctuation of a light absorbing material. The first reports of the PA effect by Alexander G. Bell in the late 1800s described the generation of sound from macroscopic solids exposed to a modulated white light source.¹ However, limitations in light generation capabilities and detection efficiency hindered development of PA-based technology over much of the ensuing century. This changed in the late 1960s (following the invention of the first ruby lasers) with a rapid development of PA spectroscopy as the basis for highly sensitive analytical methods for both gas and condensed phase materials.²

In this paper, we present the single-particle photoacoustic spectrometer (SP-PAS), with which photoacoustic measurements of single particles ranging in size from 0.3 to 10 μm radius can be made. As has been already noted in the literature,^{3–8} single-particle studies benefit from the ability to measure size-dependencies of physical and chemical properties that may be otherwise obscured by ensemble measurements. The combination of the sensitivity of photoacoustic detection with the size-sensitivity of single-particle methods opens up new possibilities for the measurement of physical, optical, and chemical properties in individual droplets, with applications towards atmospheric chemistry, bioanalytics, etc.

In the following sections, we describe the SP-PAS, its design, sensitivity, and capabilities. We conclude with two examples of experiments made possible by this new instrument.

2. EXPERIMENTAL METHODS

The single particle PA measurements presented here were carried out using a setup that deviated only slightly from a previously published design.⁷ The model aerosol studied was a cyano-based dye dissolved in tetraethylene glycol (Vis441/TEG). An intensity-modulated, blue laser was used to excite the electronic transition of Vis441. Additional long term experiments were performed on pure TEG droplets using an intensity-modulated infrared excitation laser at 9.47 μm , which is tuned to the CO absorption of TEG. Operation of the SP-PAS may be separated into three main tasks: (1) sample introduction; (2) particle trapping; (3) excitation and detection of photoacoustic signal.

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Figure 1. Schematic of the single-particle photoacoustic spectrometer. A single aerosol droplet is immobilized within the photoacoustic resonance chamber by counter-propagating optical tweezers (red lines). The photoacoustic excitation source is either the 450 nm or the 9.47 μm laser. The photoacoustic response is measured with a microphone mounted inside the resonance chamber. Elastically scattered light from the blue laser by the trapped droplet is recorded with a camera mounted above the photoacoustic cell and is used for particle sizing.

2.1 Aerosol generation

Vis441/TEG solution droplets and pure TEG droplets were generated with a medical nebulizer (PARI); bottled nitrogen gas provided a backing pressure of 1.5 bar to the nebulizer. The refractive index at 450 nm of the prepared 4.5 g L⁻¹ Vis441 solution is $1.46 + i0.0062$. The refractive index of pure TEG droplets at 9.47 μm is $1.4 + i0.2$. A short (≈ 0.5 s) pulse of aerosol from the nebulizer is carried into the photoacoustic chamber by a controlled nitrogen flow of 2 mL min⁻¹. From this pulse, a single droplet is captured at random by the optical trap. The remaining aerosol is flushed from the photoacoustic chamber with dry nitrogen gas. During the flushing period, the trapped particle often grows by coagulation with other droplets.

2.2 Optical trap

The optical trap (Figure 1) is formed by a laser (Laser quantum, Opus 660) operating at a wavelength of 660 nm at 500 mW power. A half-wave plate (HWP) is used to rotate the polarization of the beam to approximately 45°, after which the beam is split into two, cross-polarized beams with a polarizing beam splitter (PBS); small adjustments in the relative power of the two beams can be made by rotating the HWP. The two beams form a counter-propagating optical tweezer, which can trap effectively using low numerical aperture (NA) lenses, making it compatible with a photoacoustic resonator.⁹ Aspherical lenses (L3 and L4) with a focal length of 78 mm form the trap. A microscope objective (Mitutoyo 20X long WD, NA=0.42) mounted above the trap projects an image of the angle-dependent, elastically scattered light^{10,11} from the 450 nm laser onto a CMOS camera (ThorLabs, DCC1545M). These images allow simultaneous monitoring of both particle size and position within the trap.

2.3 Photoacoustic measurement

Photoexcitation of the immobilized Vis441/TEG droplets was performed with a 4000 Hz, sine-wave-modulated, 450 nm diode laser (Thorlabs, LP450-SF15) at 1 mW power. TEG droplets were excited at the same modulation frequency using a 9.47 μm distributed feedback, quantum cascade laser (Adtech Optics, CM7-CIA082). The PA response from the droplets is amplified via an acoustic resonance of the PA chamber.^{7,9} The resulting sound

wave was picked up by an electret microphone (Knowles, EK 23029) positioned just below the particle and at an antinode of the PA resonator. After preamplification it was digitized by a digital lock-in amplifier (Stanford Research, SRS 830) with a time constant of 100 ms.

3. RESULTS AND DISCUSSION

The stability, sensitivity, and size-selectivity of the SP-PAS make this analytical setup unique amongst photoacoustic instruments in general, and play a critical role in our ability to probe chemical and physical processes within single droplets. In the following section, the performance of the instrument is first discussed, followed by two examples of experiments that highlight the unique capabilities of this instrument.

3.1 Characterization of SP-PAS performance

Two complementary experiments were conducted to characterize instrument performance. In one experiment, the visible light absorption of singly trapped Vis441/TEG droplets was measured. In a second experiment a single TEG droplet was trapped and its absorption at 9.47 μm was monitored to assess long-term droplet stability within the trap.

The SP-PAS combines an optical trap with photoacoustic detection. After amplification, the typical PA signal levels range from tens to hundreds of microvolts (for Vis441/TEG droplets) depending on the size and absorption cross-section of the droplets. The background noise was assessed at 1.8 μV using a lock-in amplifier time constant of 100 ms. This sensitivity enables the measurement of attogram amounts of chromophore, dissolved in droplets smaller than 300 nm, and with a time resolution of less than one second.

The optical trap is composed of two counter-propagating, focused Gaussian beams whose foci intersect at the particle trapping position (Fig. 1). The trap must be strong enough to counteract external forces that act on the particle, such as aerodynamic drag and photophoretic forces. In the trap, there is always an unavoidable drag force of a few pN arising from the flow of nitrogen used as a purge gas throughout the experiment.

It is critical that the reproducibility of the trapping position is high enough to ensure that the droplets are always trapped inside the excitation beam. The observed positional variability of scattering image on the CMOS camera indicates a trapping stability along the axis of the trapping beams of approximately 10 μm . Variability in trapping position cross-axis is insignificant. Also, when the excitation laser is switched on, the particles experiences new forces and small positional changes can occur.

A result of the small variability in trapping position is that the excitation beam focus has an effect on the signal stability (Fig. 2). We observe greater scatter in the data collected with a focused excitation beam compared to a beam that is slightly defocused (Fig. 2b). The source of this scatter is illustrated by the corresponding beam profiles in Fig. 2a. The gray-shaded region indicates the positional variability of the trapped particle with respect to the excitation beam. Clearly, the particle experiences very different light intensities depending on its position within the trapping region. Moving the focus away from the particle flattens the beam profile and reduces the scattering in absorption measurements.

Fig. 3 shows the photoacoustic signal from a single particle recorded over many hours. It reveals the particle's response to changes in both the photoacoustic excitation and the droplet's local environment. At event **A** the infrared (9.47 μm) excitation laser is turned on and the trapped particle is heated, causing it to shrink due to slow evaporation of TEG. This results in a decrease in the photoacoustic signal. When the excitation laser is switched off (events **B** and **D**) the particle cools, lowering its vapor pressure and initiating slow growth due to condensation from residual gas phase TEG.^{8,10} This growth is evidenced by a slightly stronger signal at events **C** and **E**, when the excitation laser is switched back on. The final stability of the photoacoustic signal between events **C** and **D** indicates that the particles has reached a dynamic equilibrium with its gas phase surroundings and is no longer changing. At **F** the trapping laser is switched off and the particle flushed out. The remaining photoacoustic signal reflects a contribution from the residual gas phase TEG. Flushing the photoacoustic chamber with a high nitrogen gas flow (event **G**) decreases the signal to the instrument background level. (**G**). This sequence of events illustrates the long term stability of the trapping and photoacoustic response.

Figure 2. Effect of the 450 nm excitation laser beam focus upon the single-particle photoacoustic spectrometer signal. (a) Theoretical intensity cross-sections of two differently-focused laser beams at the particle position. A focused (orange) and slightly defocused (blue) beam is shown. The estimated size of the trapping region is indicated in gray. (b) Photoacoustic absorption measurements of particles between 0.7 and 5 μm taken with a focused (orange) and defocused (blue) beam. The increased scatter in the data taken with a focused excitation beam indicates different local intensities for different particles.

Figure 3. Response to changes in experimental conditions of the photoacoustic signal from a TEG droplet. Each event corresponds to sharp transitions in signal. There are seven events in total. The first event, **A**, corresponds to turning on the modulated IR. The subsequent decrease in signal corresponds with shrinking of the TEG droplet. Between events **B** and **C**, turning off and on, respectively, of the IR, the droplet increased in size slightly, evidenced by the slightly stronger signal immediately after **C** compared with the signal just prior to **B**. Similar behavior is observed through events **D** and **E**. After removal of the droplet from the trap (**F**) a mean background signal of approximately 0.65 μV was recorded. The final event, **G**, corresponds to an increase in nitrogen gas flow through the photoacoustic cell. The resulting decrease in signal reveals that a photoacoustically active species (likely TEG vapor) remains in the cell even in the absence of a liquid phase droplet.

In conclusion, the main experimental advance is the combination of photoacoustic detection with optical trapping. The demand on the trapping mechanism is a strong restoring force, a high confinement and a reproducible trapping position within a few microns, while still leaving space for an acoustic resonator and imaging optics. These demands are met by our counter-propagating optical tweezers. One of the challenging aspects of the long term experiments is the occurrence of small drifts in the pointing of the trapping lasers. These drifts, as well as changes in particle size, leads to small fluctuations in the trapping position, which, as illustrated earlier (Fig. 2), result in a decrease in the reproducibility of photoacoustic measurements. Incorporation of active feedback control of the trapping lasers could surmount this challenge.

3.2 Size dependence of photoacoustic response

Over the past couple decades, photoacoustic methods have been developed for the measurement of aerosol light absorption.^{12–20} Physical models have been developed for the PA process within aerosols^{8,21–24} to account for the effects of particle thermal inertia upon the droplet PA response. The models indicate a particle size-sensitivity of the PA response, however, this phenomenon has not previously been experimentally verified.

Figure 4. Measured (circles) and modeled (line) photoacoustic response from Vis441/TEG droplets.⁸

The signal stability and sensitivity of our SP-PAS, as described in Sec. 3.1, along with the size-sensitivity afforded by single particle experiments, has enabled the first experimental examination of the effect of particle size upon the photoacoustic response.⁸ We examined the photoacoustic response from a series of individual Vis441/TEG particles (Fig. 4). There is good agreement between our measured response and the model-predicted response over approximately one order of magnitude of particle radius.

These results give an experimental confirmation of the theoretical framework, improving confidence in photoacoustic absorption measurements of fine soot aerosols and opening up the possibility to correct photoacoustic field and laboratory measurements for biases experienced during measurement of light absorption by larger aerosol particles.

3.3 Droplet photokinetics

Photochemical processes within the aerosol phase play an important role in the transformation of chemical species, both inorganic and organic, in the atmosphere.^{25,26} Atmospheric modeling efforts that seek to include a photochemical component can benefit from fundamental, laboratory-based measurements of photochemical rates of reaction. However, electric field enhancement within droplets, due optical cavity resonances,²⁷ could lead to reaction rates within droplets that are increased compared with those measured in the bulk phase.

Figure 5. Measured (circles) and modeled (blue line) photolysis rates of Vis441 in TEG droplets.

By measuring the time-dependent photoacoustic response from single Vis441/TEG droplets, we were able to determine the photobleaching rates of Vis441 in the particles when exposed to a 450 nm laser.⁷ We found a significant dependence of photobleaching rates upon particle radius (Fig. 5), with particles of approximately 1 μm in radius bleaching at more than twice the rate of larger particles. A model developed to predict the size-dependence of the photobleaching process agrees with our observations. The same model, applied to water droplets over a range of wavelengths (i.e. real-world, atmospheric conditions), indicates rates of photochemical reactions in sub-micron sized droplets of up to 10-fold greater than in bulk solution. This result stresses the importance of accounting for droplet size in global atmospheric chemistry models.

4. CONCLUSIONS

We have developed an instrument to measure the photoacoustic response from single, optically-trapped aerosol droplets. Careful tuning of the trapping optics and photoacoustic excitation optics have yielded signal sensitivity and stability that allows for detailed investigations of particle physics and chemistry. Using this instrument, we have studied the fundamental physics underlying the photoacoustic process within aerosols, confirming earlier theoretical descriptions of the process. We have also measured, for the first time, an enhancement of photochemical rates of reaction in small droplets compared with bulk reaction rates. This has set the stage for future studies of aerosol physical, chemical, and optical properties that will benefit from the unique features of the instrument.

ACKNOWLEDGMENTS

This work was supported by the ETH Zürich and the Swiss National Science Foundation (SNSF).

REFERENCES

- [1] Bell, A. G., "On the production and reproduction of sound by light," *Am. J. Sci.* **20**(118), 305–325 (1880).
- [2] Haisch, C., "Photoacoustic spectroscopy for analytical measurements," *Meas. Sci. Technol.* **23**(1), 012001 (2012).
- [3] Krieger, U. K., Marcolli, C., and Reid, J. P., "Exploring the complexity of aerosol particle properties and processes using single particle techniques," *Chemical Society Reviews* **41**(19), 6631 (2012).

- [4] Mason, B. J., King, S.-J., Miles, R. E. H., Manfred, K. M., Rickards, A. M. J., Kim, J., Reid, J. P., and Orr-Ewing, A. J., "Comparison of the accuracy of aerosol refractive index measurements from single particle and ensemble techniques," *J. Phys. Chem. A* **116**(33), 8547–8556 (2012).
- [5] Lu, J. W., Isenor, M., Chasovskikh, E., Stapfer, D., and Signorell, R., "Low-temperature Bessel beam trap for single submicrometer aerosol particle studies," *Review of Scientific Instruments* **85**, 095107 (2014).
- [6] Lu, J. W., Rickards, A. M. J., Walker, J. S., Knox, K. J., Miles, R. E. H., Reid, J. P., and Signorell, R., "Timescales of water transport in viscous aerosol: Measurements on sub-micron particles and dependence on conditioning history," *Phys. Chem. Chem. Phys.* **16**(21), 9819–9830 (2014).
- [7] Cremer, J. W., Thaler, K. M., Haisch, C., and Signorell, R., "Photoacoustics of single laser-trapped nanodroplets for the direct observation of nanofocusing in aerosol photokinetics," *Nat. Commun.* **7**, 10941 (2016).
- [8] Cremer, J. W., Covert, P. A., Parmentier, E. A., and Signorell, R., "Direct measurement of photoacoustic signal sensitivity to aerosol particle size," *J. Phys. Chem. Lett.*, doi 10.1021/acs.jpcllett.7b01288 (2017).
- [9] A. Miklós, P. H., "Application of acoustic resonators in photoacoustic trace gas analysis and metrology," *Rev. Sci. Instr.* **72**(4), 1937–1955 (2001).
- [10] Davis, E. J. and Schweiger, G., [*The Airborne Microparticle: Its Physics, Chemistry, Optics, and Transport Phenomena*], Springer-Verlag, Berlin (2002).
- [11] Bohren, C. F. and Huffman, D. R., [*Absorption and Scattering of Light by Small Particles*], Wiley-Interscience, New York (1998).
- [12] Arnott, W. P., Moosmüller, H., Rogers, C. F., Jin, T., and Bruch, R., "Photoacoustic spectrometer for measuring light absorption by aerosol: Instrument description," *Atmos. Environ.* **33**(17), 2845–2852 (1999).
- [13] Lack, D. A., Lovejoy, E. R., Baynard, T., Pettersson, A., and Ravishankara, A. R., "Aerosol Absorption Measurement using Photoacoustic Spectroscopy: Sensitivity, Calibration, and Uncertainty Developments," *Aerosol Sci. Technol.* **40**(9), 697–708 (2006).
- [14] Ajtai, T., Ágnes Filep, Schnaiter, M., Linke, C., Vragel, M., Bozóki, Z., Szabó, G., and Leisner, T., "A novel multi-wavelength photoacoustic spectrometer for the measurement of the UV–NIR spectral absorption coefficient of atmospheric aerosols," *J. Aerosol Sci.* **41**(11), 1020–1029 (2010).
- [15] Bueno, P. A., Havey, D. K., Mulholland, G. W., Hodges, J. T., Gillis, K. A., Dickerson, R. R., and Zachariah, M. R., "Photoacoustic measurements of amplification of the absorption cross section for coated soot aerosols," *Aerosol Sci. Technol.* **45**(10), 1217–12230 (2011).
- [16] Haisch, C., Menzenbach, P., Bladt, H., and Niessner, R., "A Wide Spectral Range Photoacoustic Aerosol Absorption Spectrometer," *Anal. Chem.* **84**, 8941–8945 (2012).
- [17] Sharma, N., Arnold, I. J., Moosmüller, H., Arnott, W. P., and Mazzoleni, C., "Photoacoustic and nephelometric spectroscopy of aerosol optical properties with a supercontinuum light source," *Atmos. Meas. Tech.* **6**(12), 3501–3513 (2013).
- [18] Wiegand, J. R., Mathews, L. D., and Smith, G. D., "A UV–Vis Photoacoustic Spectrophotometer," *Anal. Chem.* **86**(12), 6049–6056 (2014).
- [19] Radney, J. G. and Zangmeister, C. D., "Measurement of gas and aerosol phase absorption spectra across the visible and near-IR using supercontinuum photoacoustic spectroscopy," *Anal. Chem.* **87**(14), 7356–7363 (2015).
- [20] Langridge, J. M., Richardson, M. S., Lack, D. A., and Murphy, D. M., "Experimental evidence supporting the insensitivity of cloud droplet formation to the mass accommodation coefficient for condensation of water vapor to liquid water," *Geophys. Res. Lett.* **43**, 6650–6656 (2016).
- [21] Baker, M., "Energy absorption by volatile atmospheric aerosol particles," *Atmos. Environ.* **10**(3), 241–248 (1976).
- [22] Arnott, W. P., Moosmüller, H., Sheridan, P. J., Ogren, J. A., Raspet, R., Slaton, W. V., Hand, J. L., Kreidenweis, S. M., and Collett, J. L., "Photoacoustic and filter-based ambient aerosol light absorption measurements: Instrument comparisons and the role of relative humidity," *J. Geophys. Res. Atmos.* **108**(D1), AAC15-1–15-11 (2003).
- [23] Raspet, R., Slaton, W. V., Arnott, W. P., and Moosmüller, H., "Evaporation–condensation effects on resonant photoacoustics of volatile aerosols," *J. Atmos. Oceanic Technol.* **20**(5), 685–695 (2003).

- [24] Murphy, D. M., “The Effect of Water Evaporation on Photoacoustic Signals in Transition and Molecular Flow,” *Aerosol Sci. Technol.* **43**, 356–363 (2009).
- [25] George, C., Ammann, M., D’Anna, B., Donaldson, D. J., and Nizkorodov, S. A., “Heterogeneous Photochemistry in the Atmosphere,” *Chem. Rev.* **115**(10), 4218–4258 (2015).
- [26] Herrmann, H., Schaefer, T., Tilgner, A., Styler, S. A., Weller, C., Teich, M., and Otto, T., “Tropospheric Aqueous-Phase Chemistry: Kinetics, Mechanisms, and Its Coupling to a Changing Gas Phase,” *Chem. Rev.* **115**(10), 4259–4334 (2015).
- [27] Benincasa, D. S., Barber, P. W., Zhang, J.-Z., Hsieh, W.-F., and Chang, R. K., “Spatial distribution of the internal and near-field intensities of large cylindrical and spherical scatterers,” *Appl. Opt.* **26**, 1348–1356 (1987).