



Supplement of

Photo-induced shrinking of aqueous glycine aerosol droplets

Shinnosuke Ishizuka et al.

Correspondence to: Ruth Signorell (rsignorell@ethz.ch) and Shinnosuke Ishizuka (ishizuka.shinnosuke.a3@f.mail.nagoya-u.ac.jp)

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S1 Control measurements with photochemically inert droplets

The shrinking of the aqueous glycine droplets reported in the main text indicates a photochemical reaction of glycine with the incident light. For comparison, similar measurements were performed on aqueous sea salt droplets, which are photochemically inert at visible wavelengths. The droplets are generated from aqueous solution containing commercially available sea salt (Sigma-Aldrich, SSWS500) and purified water (resistivity 18.2 M Ω -cm). The light scattering intensity (“Total TAOS”) is plotted in Fig. S1a over a period of approximately 15 h. The laser power for this measurement was 2 W. In contrast to the measurements of glycine droplets, the scattering intensity of sea salt droplets remains largely constant over the whole duration. The small changes in intensity that are observed during the time interval are due to drifts of the RH in the cell and the corresponding change in the water content of the droplet, which leads to small size changes. Compare this data to Fig. 3 in the main text, where due to the droplet shrinking, multiple Mie resonances are observed in a similar time interval. The data in Fig. S1a shows that for optically trapped aqueous sea salt droplets, no relevant size changes are observed over a time period of 15 h.

Since aqueous sea salt droplets are only weakly absorbing in the near UV/vis range, the droplet size can be accurately measured using our broad-band light scattering (BLS) setup (David et al., 2016; Reich et al., 2020), providing additional size data. The radius of the droplet is measured at the start and the end of the specified time interval, and the values agree very well with each other (Fig. S1b). Thus it is seen, that photochemically inert droplets do not shrink when optically trapped.

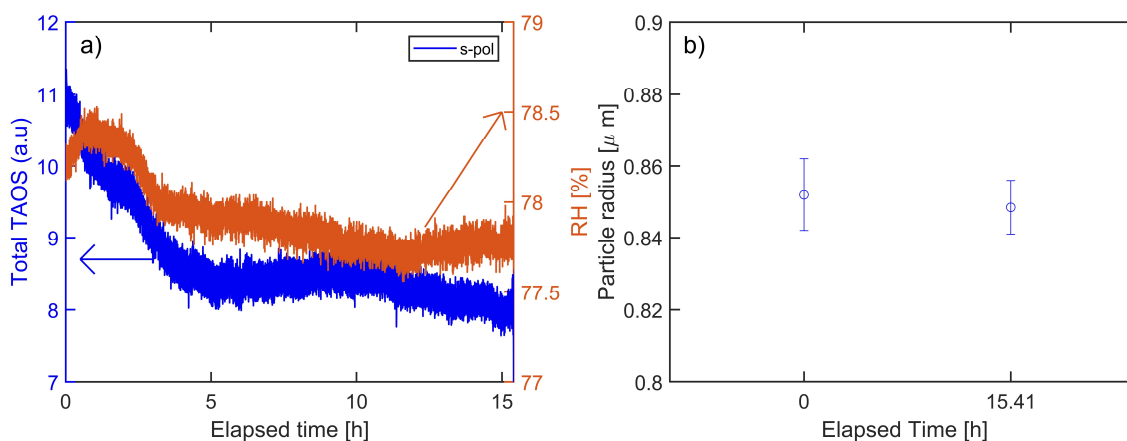


Figure S1 Light scattering of aqueous sea salt droplets over time. **a)** Total TAOS signal over time. The RH data indicates small drifts of the RH in the cell over the course of the measurements. **b)** Radius of the droplet determined by BLS at the start and end of the time interval in **a)**. The error bars indicate the BLS fit uncertainties as specified in our previous work (Reich et al., 2020).

S2 Light absorption by a microscopic water droplet

This section presents an upper estimate for the temperature increase of an optically trapped glycine droplet due to light absorption. For the following calculations we assume that the droplet contains only water, as the overall light absorption by aqueous glycine is negligible in comparison. The cross-section of the light absorption by a microscopic sphere can be calculated using Mie theory:

$$C_{\text{abs}} = C_{\text{ext}} - C_{\text{sca}}$$
$$C_{\text{sca}} = \frac{\lambda^2}{2\pi} \sum_n (2n + 1)(|a_n|^2 + |b_n|^2)$$
$$C_{\text{ext}} = \frac{\lambda^2}{2\pi} \sum_n (2n + 1)(\text{Re}(a_n) + \text{Re}(b_n))$$

where λ is the wavelength of the light and a_n and b_n are the scattering coefficients (Bohren and Huffman, 2008). The refractive index of water at $\lambda = 532$ nm is approximately (Hale and Querry, 1973)

$$N_{\text{H}_2\text{O}} = 1.334 + i \cdot 1.5 \cdot 10^{-9}$$

Using $N_{\text{H}_2\text{O}}$, $\lambda = 532$ nm and the range of the radii of our droplets, $R = 1 - 3$ μm , one obtains a typical value of the absorption cross-section of

$$C_{\text{abs}} = 2 \cdot 10^{-18} \text{ m}^2$$

The incident light intensity can be estimated by assuming a total power of $P_0 = 1$ W and an area of $A = (3\mu\text{m})^2$ (the area of the beam waist). The values of P_0 and A are generous estimates for our setup and lead to an upper limit for the temperature increase.

The absorption rate of the droplet is

$$W_{\text{abs}} = \frac{P_0}{A} \cdot C_{\text{abs}} = 2.2 \cdot 10^{-7} \text{ W}$$

Let T_1 be the temperature of the droplet and T_∞ the temperature far away from the droplet, i.e. room temperature. The total heat flow from the particle into the surrounding can be calculated using

$$Q = 4\pi r^2 \cdot q(r)$$

where $q(r)$ is the heat flux in radial direction at distance $r \geq R$ from the center of the particle. The equation for the heat flux in radial direction is

$$q(r) = -k \cdot \frac{\partial}{\partial r} T$$

where k is the thermal conductivity. The value of the thermal conductivity at the droplet/air interface is at least equal to the thermal conductivity of air at room temperature, $k_{air} = 0.025 \text{ W m}^{-1}\text{K}^{-1}$. In addition, we neglect convection and radiative energy transfer for our upper estimate of the temperature increase.

Thus we obtain for $r \geq R$

$$q(r) = \frac{Q}{4\pi r^2} = -k \cdot \frac{\partial}{\partial r} T$$
$$\Leftrightarrow T(r) = \frac{Q}{4\pi k} \frac{1}{r} + C$$

At $r \rightarrow \infty$ the temperature must be equal to the room temperature, thus one obtains

$$C = T_\infty$$

The heat conduction inside the droplet is much faster than the heat conduction in the surrounding gas, due to the comparatively large heat conductivity of water. Therefore, we assume that the temperature is approximately constant everywhere inside the droplet. With this, the temperature of the particle is obtained as

$$T_1 = T(R) = \frac{Q}{4\pi k} \frac{1}{R} + T_\infty$$

In the steady state, the total heat flow Q is equal to the absorption rate of the particle W_{abs} . This gives us an upper estimate of the difference between droplet and room temperature:

$$T_1 - T_\infty \leq \frac{W_{abs}}{4\pi k_{air}} \frac{1}{R} = 0.7 \text{ K}$$

Supplementary references

Bohren, C. F. and Huffman, D. R.: Absorption and scattering of light by small particles, John Wiley & Sons, ISBN 978-0-471-29340-8, 2008.

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