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Photoacoustics of single aerosol droplets immobilised by counter-propagating optical tweezers

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ABSTRACT

In this contribution we discuss the influence of relative humidity on photoacoustic measurements from both an experimental and theoretical perspective. We present a refined model of the photoacoustic (PA) signal that accounts for elevated particle temperatures and different levels of relative humidity. We use this new model together with the photoacoustic data collected with our photothermal single-particle spectrometer (PSPS) to retrieve the mass accommodation coefficients of water on organic aerosol particles. The single-particle nature of our experiments is achieved by employing counter-propagating tweezers. Furthermore, we investigate the influence of relative humidity on the eigenfrequency of the PA cell.

Keywords: photoacoustic spectroscopy, optical trapping, counter-propagating tweezers, mass accommodation coefficient, aerosols, relative humidity

1. INTRODUCTION

Aerosol particles are ubiquitous in the atmosphere and thus influence the global climate^{1–5} and human health.^{6–9} Light absorption and scattering by aerosol particles influences the climate directly, while their ability to behave as cloud-condensation nuclei govern the cloud formation, by which they indirectly influence the climate and weather patterns. Aerosol particles represent a highly complex system to study due to their different compositions (ranging from organic droplets to inorganic salts), wide size distributions (nanometre to micrometre range), different phases and various morphologies. Strong coupling between the gas and condensed phase influences the aerosols' physical-chemical properties on a variety of timescales, ranging from seconds to days.^{10–12} As a result, aerosols represent one of the major uncertainty in current climate modelling.^{1–5} Due to the abundance of water vapour in the atmosphere, water uptake by aerosol particles plays a key role in defining the overall effect of aerosols on the climate. The uptake of water by various organic and inorganic aerosols influences their composition, size and ultimately their scattering albedo (the ratio of the scattering coefficient to the total extinction coefficient). As a result, studies of water transport between the gas and aerosol phase have received a lot of attention recently.

Upon collision with a liquid or solid surface, gas phase molecules can either reflect from the surface or get adsorbed and therewith enter the corresponding condensed phase (heterogeneous uptake of water). The competition between the reflection and adsorption governs the ability of aerosols to nucleate cloud droplets and thereby controls the droplet number density.^{1,2,5,13,14} The fraction of gas-phase molecules that stick to the surface upon collision is described by the mass accommodation coefficient α_M ,^{15–17} which is a probability value and takes on values between 0 and 1. It was defined as early as 1859 by Maxwell in his papers on the dynamical theory of gases¹⁸ and, under microscopic reversibility, equals the evaporation coefficient.^{16,19} Mass accommodation coefficients are important for accurate modelling of the kinetic growth rates of aerosol particles induced by the uptake of gas phase species, such as water. Reliable values of α_M are crucial in the areas of climate modelling,^{1,20} aerosol drug delivery^{21,22} and many industrial applications, such as ink-jet printing or electrospraying. However, accurate values of mass accommodation coefficients are still lacking for many systems. For example, the values of α_M for the well-studied system of water on water span orders of magnitude.^{23–25} Consequently, it is important to design new experimental techniques that can be used to retrieve reliable values of the mass accommodation coefficients.

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Photoacoustic (PA) spectroscopy is a highly sensitive absorption technique used routinely in research field campaigns^{26–31} and in laboratories,^{32–37} for example, to quantify the absorption or monitor the concentration of specific gas phase species or aerosol particles. The main principle of PA spectroscopy is conversion of light energy into acoustic energy (sound). This is achieved by using intensity-modulated laser light that is absorbed by the studied system, which in turn induces an energy flux from the particle to the surrounding gas phase (Figure 1). One pathway of energy exchange with the ambient gas is through direct collisions between the surrounding gas and the particle surface (heat flux). Another pathway involves evaporation and condensation of volatile species (mass flux). The overall energy flux from and to the particle gives rise to the formation of pressure waves that can be measured using a microphone or a tuning fork.^{38–43} The mass flux is dependent on the mass accommodation coefficient. Thus, by performing the photoacoustic measurements at different levels of relative humidity, the values of the mass accommodation coefficients of water on organic aerosol can be retrieved.

Figure 1. An illustration of the photoacoustic effect. An aerosol particle (blue) is irradiated with an intensity-modulated IR laser (red) which results in heat flux and mass flux, both of which constitute the photoacoustic signal.

In order to study the properties of aerosols on a fundamental level, single-particle methods are often employed. Studying single particles as opposed to ensembles avoids ensemble averaging effects^{44–46} and allows for size-specific measurements performed in tightly controlled environmental conditions (temperature and relative humidity). Optical traps^{47–52} are routinely used to levitate a single droplet in air, as they allow for convenient working distance, tight confinement and do not introduce any morphological changes to the trapped droplets. Optical trapping has been used in the past, for example, to measure refractive indices of aerosols,^{53–59} collect Raman spectra^{60–62} or measure viscosity⁶³ and surface tension.⁶⁴ Cremer et al. developed the first single-particle photoacoustic spectrometer, which allows for size specific PA measurements on optically trapped droplets.^{32,65,66}

In our previous work, we investigated the influence of relative humidity on the PA signal^{33,34,67} which has been long discussed in the literature.^{27,29,35,68} Using the relative humidity dependence of the PA signal, we were also able to retrieve the mass accommodation coefficients of water on organics.^{69,70} In this work we further investigate the influence of relative humidity on the acoustic properties of the PA cells and we present a new theoretical model, which allows for simulations of particles with elevated temperatures at different levels of relative humidity. We use this newly revised model to retrieve the mass accommodation coefficients from our previously collected experimental data.^{33,34}

2. METHODS

2.1 Experimental

The measurements were performed using our single-particle photoacoustic set-up,³² shown in Figure 2. Here, only a brief description of the set-up is provided, as the details can be found elsewhere.^{33,34,69} We use a

532 nm laser (Laser Quantum, Opus, continuous wave) to build a counter-propagating optical trap by first splitting the beam into two equal parts using a polarisation beam splitter cube (PBC, PBS201 Thorlabs). The two trapping laser beams (each ~ 250 mW) are focused inside the PA cell with a facing pair of aspherical lenses (75 mm, ASL10142 Thorlabs). An IR laser (9.47 μm diode laser from AdTech Optics) is focused inside the PA cell by a ZnSe lens (75.0 mm, LA7660-G, Thorlabs), perpendicular to the direction of the trapping laser.

Figure 2. A sketch of the experimental set-up, showing the trapping laser (green), photoacoustic laser (gray) and the PA cell (yellow).

The photoacoustic cell consists of an acoustic resonator (4 cm long and 4 mm in diameter) attached to two buffer volumes (1.5 cm long and 3 cm in diameter) at either side of the resonator. The acoustic resonator is designed such that it amplifies longitudinal acoustic modes at 4000 Hz. The buffer volumes behave as noise-cancellers, thus their design strongly influences their performance.^{71,72} The signal is generated by illuminating a trapped particle by the intensity-modulated IR laser, which results in a photoacoustic effect. The sound wave produced by the trapped particle is measured using an electret microphone (Knowles Electronics, EK-23133-C36), which is located directly below the particle at an antinode of the excited acoustic mode. The microphone signal is amplified by a self-made amplifier and detected using a lock-in amplifier (Zurich Instruments, 500 kHz MFLI) that demodulates the input signal at 4000 Hz.

The PA cell allows for optical trapping, photoacoustic measurements and light scattering measurements to be carried out simultaneously. The scattered 532 nm light is collected using a microscope objective (Mitutoyo, M Plan Apo 20x Objective), which is located on top of the cell, and then projected onto a CMOS camera, photodiode (Hamamatsu, S2506-02) and a quadrant photodiode (Hamamatsu, S5980). The camera signal is used for visual control of the particle, the photodiode signal is used for size determination⁵² and the quadrant photodiode is used for feedback stabilisation of the trapped particle.³³ The feedback loop drives the electro-optical modulator (EOM, 350-50-01, ConOptics) that is attached to an adjustable mount (M102A, ConOptics) for a perfect alignment. A home-built proportional-integral-derivative (PID) controller adjusts the voltage applied to the EOM depending on the signal from the quadrant photodiode, effectively altering the polarisation of the trapping beam prior to the PBC. As a consequence, the respective powers of the two beams after passing through the polarisation beamsplitter are changed. This feedback loop greatly stabilises the position of the trapped particle and guarantees a consistent trapping position for differently sized particles.

The aerosol particles composed of tetraethylene glycol (TEG) are produced using a medical nebuliser (Pari LC Sprint). TEG serves as a good model material for hydrophilic organic aerosols, although ethylene glycols themselves are not an important component of the particulate matter in the atmosphere. A pulse of generated aerosol droplets is brought into the PA cell, where one particle gets trapped in the focal region of the trapping beams. Nitrogen gas (20 sccm) is used to remove the excess of aerosols and to control the relative humidity. Measurements on TEG particles were performed at different levels of relative humidity, ranging from 11 % to 93 % achieved by mixing dry and wet flows of nitrogen. The analysis of the photoacoustic and scattering signals from TEG particles enables us to retrieve the mass accommodation coefficient which are presented in Section 3.3.

In order to investigate the acoustic properties of the PA cells, measurements on the background signals were collected. The background signals most likely originate from the aerosol deposition on the BaF₂ windows, through which the IR laser enters the PA cell. During these measurements, the PA cell contained no trapped particle. Figure 3 shows an eigenfrequency sweep of our PA cell. We observe an acoustic resonance at ~3900 Hz. The PA amplitude is fitted using a Lorentzian function (Figure 3 right), from which the eigenfrequency of the acoustic resonator can be retrieved. Similarly, the first derivative of the PA phase can be fitted with a Lorentzian.

Figure 3. Left: an eigenfrequency sweep of the PA cell at 45 %RH, showing the PA amplitude and phase components. The PA amplitude and phase are clearly related, with the maxima in the PA amplitude coinciding with the inflexion point in the PA phase. Right: raw experimental PA amplitude data fitted with a Lorentzian function.

2.2 Modelling

Our model is based on the theory proposed by Kulmala et al.,^{25,73–76} which was also adopted by Murphy⁷⁷ and successfully used in our former work.^{33,34,69} It comprises a locally fixed, spherical particle composed of aqueous TEG with its composition varying with relative humidity, and an IR laser tuned to be absorbed efficiently by TEG, trapped inside an acoustic resonator with constant ambient temperature T_∞ , relative humidity φ and pressure p . The IR laser is intensity-modulated in a sinusoidal fashion, thus making the heating of the particle periodic as well. The equation for the energy conservation can be expressed as:

$$E(t, \omega) = Q(r, T) + I(r, x_a(\varphi))L + m_p c_{p,a}(x_a(\varphi)) \frac{\partial T}{\partial t} \quad (1)$$

where T is the particle temperature, t is time, ω is the angular frequency of the IR laser, $Q(r, T)$ is the heat flux (HF) away from the particle, $I(r, x_a(\varphi))$ is the mass flux (MF) away from the particle, r is the particle radius, L and $x_a(\varphi)$ are latent heat and molar concentration in the particle of the evaporating species, m_p and $c_{p,a}$ are mass and specific heat capacity of the particle. The absorbed IR-light represents the source term in the differential equation and is given by:

$$E(t, \omega) = E_0(e^{-i\omega t} + 1) \quad (2)$$

It oscillates between 0 and $2E_0$, where the absorbed energy density E_0 depends on the laser power I_0 and the particles absorption cross-section $C_{\text{abs}}(r, x_a(\varphi))$. Integration of the one-dimensional form of Fourier's law for thermal conduction over a spherical particle boundary yields the heat flux Q as a function of the particle's temperature in its simplest form:

$$Q(T) \approx 4\pi r K(T - T_\infty) \quad (3)$$

where K is the heat conductivity of the surrounding gas. Immanent evaporation and condensation processes of the volatile species are derived using Fick's first law of diffusion, where the gradient in concentration causes a mass flux I away from the particle. When the concentration is expressed in terms of the vapour pressure and temperature using the ideal gas law, the mass flux can be expressed in its general form as:

$$I(T) = 4\pi r \frac{DM_v}{R} \left[\frac{p_v(T)}{T} - \frac{p_v(T_\infty)}{T_\infty} \right] \quad (4)$$

where D is the diffusion constant in the gas phase, M_v is the molar mass of the evaporating species, R is the ideal gas constant and p_v is the partial pressure of the evaporating species. This is the point where the relative humidity φ enters the theory. While the saturation vapour pressure $p_{v,\text{sat}}$ is a function of temperature T and (ambient) pressure p , the partial pressure of water p_v scales linearly with φ and $p_{v,\text{sat}}$. In our experiment we work at constant p and thus the partial pressure of water is simply:

$$p_v(T) = \varphi \cdot p_{v,\text{sat}}(T) \quad (5)$$

Since the transport of energy and mass for particle sizes that we study is partially under kinetic control, an appropriate correction has to be applied. The thermal conductivity K and vapour diffusivity D of the continuum fluxes are modified by the multiplicative transitional correction factors for heat transfer β_T , and mass transfer β_M , respectively*. They take the form:

$$\beta_i = \frac{1 + \text{Kn}_i}{1 + \left(\frac{4}{3\alpha_i} + 0.377 \right) \text{Kn}_i + \frac{4}{3\alpha_i} \text{Kn}_i^2} \quad \text{where } i = T, M \quad (6)$$

where Kn_i are the Knudsen numbers $\text{Kn}_T = \lambda_g/r$ and $\text{Kn}_M = \lambda_v/r$ which depend on the particle radius r and the mean free path of the gas molecules (nitrogen) λ_g and vapour molecules (water) λ_v respectively. The coefficients α_i introduced in eq. 6 are called the thermal accommodation coefficient α_T and the mass accommodation coefficient α_M . While α_T is generally assumed to be close to unity,^{19,75,76,80} the value of α_M strongly depends on the system and is in general difficult to measure, as exemplified by the wide spread of values for water on water in the literature.^{17,19,23–25,59,76,81–83}

Combining eqs. 1 - 4 allows us to solve for the particle temperature T . It is oscillating around an average particle temperature $\bar{T}$:

$$\bar{T} = \frac{C_{\text{abs}}(r, x_a) I_0}{4\pi r \beta_T K (1 + f_M)} + T_\infty \quad (7)$$

where f_M is defined as the ratio between MF and HF. However, over a complete PA cycle, the net MF of the evaporating species (water) is zero and only the evaporation of the non-volatile species (TEG) enters eq. 7. Since the vapour pressure of TEG is very low, also this steady state mass flux is negligible on the experimental time scale. Ultimately, f_M in eq. 7 is assumed to be zero for our system.

On the timescale of one PA cycle (250 μs), the particle temperature is oscillating around $\bar{T}$ with the modulation frequency ω of the IR-laser, which in turn induces oscillations in f_M . The amplitude of the temperature oscillation is denoted with ΔT and assumed to be symmetric around $\bar{T}$:

$$\Delta T = \frac{C_{\text{abs}}(r, x_a) I_0}{4\pi r \beta_T K |1 + \delta f_M - i\omega\tau|} \quad (8)$$

*Note that there is a minor confusion in the literature, with some authors referencing the value 0.337^{73,75,78} instead of 0.377 in the denominator of eq. 6. Based on the original work of Fuchs and Sutugin,⁷⁹ the correct value is 0.377.

where δf_M is the oscillation amplitude of f_M and $\tau^\dagger$ is the characteristic time constant of the particles thermal inertia, which is given by:

$$\tau = \frac{r^2 \rho_a c_{p,a}}{3\beta_T K} \quad (9)$$

where ρ_a is the particle density. From our previous work^{33,34,69} we know that $\bar{T}$ increases significantly with particle radius. The equations for HF and MF in the traditional model^{73,74,77} start to fail when used for elevated particle temperatures and need to be adapted to compensate for temperature-dependent variables.

In this work we present a *refined model for photoacoustic single-particle spectroscopy* (PSPS) that accounts for the average particle temperatures $\bar{T}$ to be higher by several Kelvins than the ambient temperature T_∞ . The critical quantity is the water vapour pressure $p_v(T)$, which, in the basic model, was assumed to scale linearly with temperature starting from the water vapour pressure at ambient temperature, $p_v(T_\infty)$. Mathematically this was realised by a restricted Taylor expansion of the Clausius Clapeyron equation around T_∞ . In the new model, we build upon this concept, however, we expand the Clausius Clapeyron equation around the average particle temperature $\bar{T}$ in order to reduce the error of the approximation. The equation is then again linearised by using only the first two terms. In this way, the new model only applies the linear scaling of water vapour pressure with temperature to the minor oscillations of $\pm\Delta T$ around $\bar{T}$:

$$p_v(T) = p_v(\bar{T}) e^{\left(\frac{LM_v}{R} \frac{T-\bar{T}}{\bar{T}^2}\right)} \approx p_v(\bar{T}) \left(1 + \frac{LM_v}{R\bar{T}^2} \Delta T\right) \quad (10)$$

Figure 4. The saturation water vapour pressure against gas temperature from the literature (solid line) [84, table 1.52], using the Taylor expansion around T_∞ (dotted line) and Taylor expansion around $\bar{T}$ (dashed line) for $T_\infty = 20.5^\circ\text{C}$ and $\bar{T} = 30^\circ\text{C}$. The red bar indicates the correction in vapour pressure of the new model.

Figure 4 illustrates the correction to the existing model. Calculating the total differential of eq. 4 together with eq. 10 gives the change in mass flux:

$$\Delta I \approx \frac{\partial I}{\partial T} \Delta T \approx 4\pi r D \beta_M \frac{M_v p_v(\bar{T})}{R} \left[\frac{LM_v}{R\bar{T}} - 1 \right] \frac{\Delta T}{(\bar{T} + \Delta T)^2} \quad (11)$$

In principle, the temperature dependence of the heat conductivity of the surrounding gas $K(T)$ should be included, as suggested by Miles et al.⁵⁹ At ambient temperatures and pressures, water is still a trace species

[†]Note that in literature slightly different definitions of τ exist. Since β_T in eq. 8 is strictly positive, it may be pulled into the modulus brackets where it cancels out in the imaginary term. In that particular formulation of ΔT , β_T does not enter the definition of τ .

in the surrounding gas phase and contributes less than 1 % to K . For this reason it is sufficient to assume a pure nitrogen atmosphere, using:

$$K(T) = 2.45109 \cdot 10^{-4} + 9.90738 \cdot 10^{-5} T - 4.47915 \cdot 10^{-8} T^2 \quad (12)$$

The change in heat flux can be obtained by plugging eq. 12 into eq. 3 and calculating the total differential. Mixed and higher order terms that arise in the total differential are neglected, since they proved to contribute less than 1 % for all attained ΔT , whereas the deviation of eq. 12 itself is given with $\pm 2\%$.⁵⁹ Considering that $T = \bar{T} + \Delta T$, the change in the heat flux reduces to:

$$\Delta Q = 4\pi r \beta_T \frac{\partial [K(T)(T - T_\infty)]}{\partial T} \Delta T \approx 4\pi r K(\bar{T}) \beta_T \Delta T \quad (13)$$

Applying the above to the ratio of the fluxes f_M and its oscillation amplitudes δf_M , eqs. 11 and 13, yield:

$$\delta f_M = \frac{\Delta IL}{\Delta Q} = \frac{D \beta_M L M_v p_v(\bar{T})}{R K \beta_T} \left(\frac{L M_v}{R \bar{T}} - 1 \right) \frac{1}{(\bar{T} + \Delta T)^2} \quad (14)$$

Both heat and mass flux from eqs. 13 and 11 respectively contribute to the overall photoacoustic signal by forming a pressure wave in the surrounding gas with an angular frequency ω . The photoacoustic signal is delayed with respect to the IR laser emission due to the particle's thermal inertia τ . As a result, the measured PA signal S is expressed as a complex quantity with an amplitude $|S|$ and phase θ , which we refer to as the photoacoustic amplitude (PAA) and photoacoustic phase (PAP) respectively:

$$|S| = \frac{R}{p} \left(\frac{\Delta Q}{M_g c_{p,g}} + \frac{\Delta I T_\infty}{M_v} \right) =: \text{PAA} \quad \text{and} \quad (15)$$

$$\theta = \arg \left(\frac{1}{1 + \delta f_M - i \omega \tau} \right) =: \text{PAP}, \quad (16)$$

where M_g and $c_{p,g}$ are molar mass and specific heat capacity of the surrounding gas (N_2). Note that δf_M enters eq. 16 as an essential parameter, while the relative humidity enters eqs. 15 - 16 through eq. 5.

3. RESULTS

3.1 Acoustic properties of the photoacoustic cell as a function of relative humidity

In order to study the effects of relative humidity on the aerosols' absorption of light using photoacoustic spectroscopy, it is essential to characterise the effects of relative humidity on the acoustic response of the PA cell. Elevated levels of RH change the speed of sound in the gas phase and as a result change the acoustic properties of the acoustic resonator inside the PA cell. In order to investigate these effects, we performed measurements on the background signal in two different PA cells with the same acoustic resonator design. Figure 5 shows the resonance frequencies of the two cells retrieved from the photoacoustic amplitude (PAA) and photoacoustic phase (PAP) as a function of relative humidity. The eigenfrequencies were retrieved from a Lorentzian fit to the PAA data and to the first derivative of the PAP data, as shown in Figure 3. We observe that in general, the eigenfrequencies of the two PA cells differ by ~ 180 Hz, despite having identical acoustic resonators. This shows that the eigenfrequency of the PA cell is very sensitive to even subtle differences in their design. The trends with relative humidity are more pronounced in cell B (on the right in Figure 5), where we observe up to 10 Hz increase of the eigenfrequency when the relative humidity increases from 10 to 95 %.

The change of the eigenfrequency with relative humidity can be calculated using the speed of sound in dry and wet nitrogen environments. The eigenfrequency of the open-open resonator is calculated as:⁸⁵

$$f_n = \frac{nc}{2(l + \Delta l)} \quad n = 1, 2, 3, \dots \quad (17)$$

Figure 5. Resonance frequencies of the two PA cells (cell A on the left and cell B on the right) plotted against relative humidity. The resonance frequencies were retrieved from the PA amplitude (black, $\diamond$) and phase (blue, $\triangle$). The measurements were performed on the background signal.

where l is the length of the acoustic resonator (40 mm), c is the speed of sound, n is the excited harmonic and Δl is the end correction, which is added to the length of the resonator for each open end. The end correction can be approximated as $\Delta l \cong 0.6r$, where r is the radius of the acoustic resonator (2 mm in our case). The speed of sound in air at 10%RH, atmospheric pressure and a temperature of 20°C is $\sim 343.49 \text{ ms}^{-1}$ and increases by a factor of ~ 1.003 when the relative humidity changes from 10% to 93%.⁸⁶ From reference 87, we can approximate the ratio between the speed of sound in nitrogen to air to be 1.034. Hence, the speed of sound in nitrogen can be approximated to be 355.18 ms^{-1} at 10%RH and 356.24 ms^{-1} at 93%. Using eq. 17, we calculate a 12 Hz shift of the eigenfrequency when the relative humidity changes from 10% to 93%. This is in agreement with the experimentally retrieved eigenfrequency shift.

Figure 6 shows the PAA and PAP as a function of relative humidity retrieved from the frequency sweeps of the acoustic resonators. The blue trace in Figure 6 represents the PAA and PAP values at the corresponding eigenfrequencies, while the orange trace represents the values retrieved at 4 kHz. The data presented was measured on the background signal (no trapped particle). The left hand side corresponds to the PA cell A with the eigenfrequency of $\sim 3900 \text{ Hz}$ (see Figure 5 left), while the right-hand side corresponds to the PA cell B with the eigenfrequency of $\sim 4080 \text{ Hz}$ (see Figure 5 right). We observe that PAA is smaller at 4 kHz than at the corresponding eigenfrequency, which is to be expected. We also observe a slight increase of PAA with RH, both at 4 kHz and at the eigenfrequency. An important remark is that the trend with RH is the same at 4 kHz and at the eigenfrequency, suggesting that no RH biases are introduced by measuring the PA signal at 4 kHz throughout the relative humidity range considered. The trends in PAA are qualitatively similar for both cells.

Regarding PAP, we observe in both cells that there is not a clear difference between the trends of the signal with relative humidity measured at the resonant eigenfrequency (blue trace) or at 4 kHz (orange trace). This is an important confirmation that the PAP measurements performed at different relative humidities are not biased when measured at fixed 4 kHz frequency. However, we observe different overall trends of PAP with RH between the two PA cells - in cell B, the phase increases with relative humidity, while the trend with RH in the cell A is not very clear. This is most likely due to the different background signals of the two PA cells, as well as due to the sharpness of the resonance and the effective Q-factor. The PAA in cell B is higher by almost an order of magnitude compared to cell A. This makes the PAP signal in cell B easy to lock in and causes less noise in the data from this cell. As a result, the PAP error bars for cell B are much smaller allowing for the trends with RH to be visible.

In theory, upon an increase of the eigenfrequency of the acoustic resonator at elevated relative humidity,

Figure 6. PA amplitude (top) and phase (bottom) values measured in two different cells (cell A on the left and cell B on the right) at the acoustic eigenfrequency (blue, $\square$) and at 4 kHz (orange, $\circ$).

the PAP measured at 4 kHz should decrease. This can be seen in Figure 3 left - upon a shift of the blue and orange traces to higher frequencies (horizontal shift to the right), the value of the PAP measured at 4 kHz decreases. Since this is not observed experimentally in Figure 6, we can conclude that the trends observed most likely originate from differing background signals at different RH, rather than from the shift of the eigenfrequency of the resonator.

Overall, we see no pronounced biases associated with the PA measurements at varying relative humidity at the fixed frequency of 4 kHz. We observe no differences in trends in the PAA and PAP with relative humidity when measured at the acoustic resonators eigenfrequency or at fixed 4 kHz. Furthermore, we do not observe the theorised effect of the eigenfrequency shift with RH on the PAP values, suggesting that this effect is minimal.

3.2 Refined model

The newly adapted model presented here is based on the Taylor expansion of the Clausius Clapeyron equation around the average particle temperature as discussed in section 2.2. Using equation 7, we can calculate the particle's average temperature and use available vapour pressure data at these temperatures.⁸⁴ Subsequently, the Taylor expansion is performed over just a few Kelvins, as the particle temperature oscillation (ΔT) is small. This makes the new model more accurate and more representative of the real experimental conditions. The theoretical results presented in Figure 7 were obtained for exemplary values of the thermal and mass accommodation coefficient and $T_\infty = 20.5^\circ\text{C}$. For α_T the value of 0.97 was selected.^{25, 77, 88} We point out that the corrections to the heat flux have only a small influence ($<5\%$) on the simulation results. Regarding the mass accommodation coefficient, a constant value of $\alpha_M = 0.1$ was chosen, which approximates the mass accommodation coefficient values of water on organics.^{33, 67, 69}

Figure 7. Comparison between the new refined model (solid lines) and the old model (dashed lines) for relative humidities 30 % (brown, $\square$), 50 % (red, $\triangle$), 70 % (orange, $\diamond$), 90 % (green, ∇). The following signals were simulated: (a) photoacoustic amplitude (PAA); (b) photoacoustic phase (PAP); (c) heat flux (HF) and (d) mass flux (MF).

Figure 7 shows a comparison between the old and new refined model. The PAA and PAP signals are normalised to $\varphi = 11\%$ of the respective model, which is the lowest accessible relative humidity of our experimental set-up and is assumed to be the dry case. At small particle radii (0.5–1.0 μm), the old and the refined model mostly overlap, since the particle's temperature is not greatly elevated.³³ At bigger particle sizes (1.0–3.0 μm) we observe deviations in all four simulated quantities.

Both PAA (Figure 7 a) and PAP (Figure 7 b) simulations show a bigger dependence on RH using the new model throughout the entire size range considered. The heat and mass flux (Figure 7 c and d) follow the same trend, with the mass flux contribution increasing substantially in the new model. Overall, the trends of PAA, PAP, HF and MF with particle size are qualitatively similar to the old model, but the dependence on RH increases. In our previous work we used the RH-dependence of PAA and PAP to retrieve the mass accommodation coefficients.^{33,69,70} Hence, we can use the refined model to retrieve new values of the mass accommodation coefficients in order to evaluate its performance.

3.3 Mass accommodation coefficient

The mass accommodation coefficients are retrieved for the system of water on tetraethylene glycol aerosols using experimental data that was presented elsewhere^{33,34,69} and applying the refined model, which is presented in this paper (section 2.2). We used tetraethylene glycol (TEG) aerosol particles as a proxy for organics. Organic aerosols constitute up to 80 % of all the particulate matter in the atmosphere,^{80,89–91} making studies on such systems of high atmospheric relevance. Furthermore, organic aerosols are routinely used for drug delivery to the lungs, but their water uptake in the human airways significantly influences the efficiency of the drug delivery.^{92–94} The experimental data comprises photoacoustic measurements of over 390 particles that

were optically trapped in the photoacoustic cell at different levels of relative humidity. The refined model lets us simulate our system closer to real experimental conditions, yet the trends and general phenomena discussed in our previous work are not altered.^{33,34} We use the new refined model to retrieve the mass accommodation coefficient (α_M) from the photoacoustic amplitude and phase, which is shown in Figure 8. Details concerning the α_M retrieval can be found in the Supporting Information of ref. 69.

Figure 8. The mass accommodation coefficient (α_M) retrieved from photoacoustic amplitude (left) and photoacoustic phase (right).

Compared to our previous work,⁶⁹ we observe a better match among the α_M values retrieved from the two independent techniques and we obtain smaller and more consistent error bars. The reduced deviations in the α_M values directly illustrate a better match of the theory and experimental data. The mass accommodation coefficient retrieved from the photoacoustic phase (Figure 8 right) shows much smaller error bars than the photoacoustic amplitude retrieval (Figure 8 left). This can be rationalised by considering the relative spacing of the PAP curves at different relative humidity (Figure 7 b), which is significantly larger than that of the PAA curves (Figure 7 a). Furthermore, through comparison of the solid and dashed lines in Figure 7 b, we see a larger relative spread of the individual PAP curves with RH compared to the previous model, which greatly benefits the fit accuracy when using the photoacoustic phase. The major issue of the α_M retrieval from the PAA data remains the size region (2.1–2.6 μm for the example values in Figure 7 a) where the individual PAA curves at specific RH overlap. In this size range, the trend of the PAA signal with RH cannot be fitted reliably. The photoacoustic phase data does not show this behaviour as the individual PAP curves do not cross in the size range (Figure 7 b).

Both techniques yield largely overlapping values of the mass accommodation coefficients with the same trends. We observe decreasing values of α_M with particle radius, which is due to elevated particle temperatures at large radii. This trend has been discussed in detail in Ref. 69. The temperature dependence of the mass accommodation coefficient can be rationalised in terms of kinetic rates of solvation and desorption of the surface adsorbed species, as proposed by Nathanson et al.⁹⁵ A thorough understanding of the temperature-dependence of α_M is crucial for example in climate modelling, where water uptake by aerosol particles differs at different altitudes in the troposphere due to a significant change in temperature.

4. CONCLUSION

In this contribution, we have discussed the influence of relative humidity on photoacoustic measurements performed on single aerosol particles. The particles were optically trapped using counter-propagating tweezers. We evaluated the effect of the change of speed of sound at different relative humidities on the eigenfrequency

of the acoustic resonators used in the photoacoustic cells. We have found a shift of up to 10 Hz in the eigenfrequency when the relative humidity changes from 10% to 93%. Furthermore, we have presented a refined model that addresses elevated particle temperatures in the photoacoustic measurements. With this new model, we retrieved the mass accommodation coefficients of water on organic aerosols, using our previously presented data.^{33,34,69} We measured two independent signals - photoacoustic amplitude and phase - that were used for the mass accommodation coefficient retrieval. Compared to the old model that we applied in the past, we observe more consistent mass accommodation coefficient retrievals among the two independent techniques and we obtain smaller and more consistent error bars. Overall, we can conclude that the new refined model, that builds upon the vapour pressure expansion centred around $\bar{T}$, is a significant improvement.

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