Sizing non-spherical, evaporating aerosol particles using "white" light resonance spectroscopy

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Abstract

We show how "white" light resonance spectroscopy can be used to measure the evaporation rate of a solid, non-spherical aerosol particle levitated in an electrodynamic balance. The vapor pressure of solid ammonium nitrate (AN), an inorganic salt of relevance for atmospheric science, is calculated and compared with the literature.

1   Introduction

In the field of atmospheric and climate science there is considerable interest in understanding the partitioning between gas and particle phase of chemical species. In particular for semi-volatile substances like ammonium nitrate or certain organic species, the partitioning will strongly influence particulate matter burden in the troposphere. In addition, it will influence the radiative properties of the aerosol and the way it participates to cloud formation and heterogeneous chemistry. In order to predict this partitioning, it is crucial to know the vapor pressure of the compounds under ambient conditions, whereas most established methods rely on high temperatures to achieve a sufficiently high vapor pressure. One possible method to assess very low vapor pressures is to measure evaporation rates of particles, by precisely sizing the particles while evaporating. Recently, we used white light Mie resonance spectroscopy [1] for sizing and measuring the evaporation rates of aqueous solution (hence spherical) aerosol particles. In the present work we extend that method to the case of a solid, non-spherical particle.

2   Experimental setup

The experimental setup used in this study has been described previously in detail [1]. A micrometer-sized aqueous solution particle is levitated in an electrodynamic balance under sufficiently dry conditions until it effloresces whereupon its evaporation under controlled ambient conditions is monitored. The 2-dimensional angular scattering pattern is recorded with a CCD camera to distinguish liquid (spherical) particles from solid (non-spherical) particles. A ball lens type point source LED is used as a "white light" source with high spatial coherence (50 μm source diameter, peak wavelength $\simeq$ 589 nm, spectral bandwidth at 50% $\simeq$ 16 nm, radiant power $\simeq$ 150 μW) using a bestform lens ($f = 32$ mm, $f\# = 2.0$) to focus the light on the levitated particle and a pierced mirror to collect the resonance spectra in a backscattering geometry (collection angle $180°\pm4°$). An optical fiber is employed to deliver the backscattered light from the particle to a spectrograph with an array detector as an optical multichannel analyzer.

3   Results and discussion

Figure 1 shows three spectra of a solid, non-spherical AN particle levitated at T=293 K taken at the different times during an evaporation experiment. The spectra show a complex structure of weak optical resonances, but a time series of spectra does not allow easily to discern a shift in the resonance position as it is the case with a spherical particle evaporating. The most pronounced difference between spectra is the different mean backscattered intensity. The
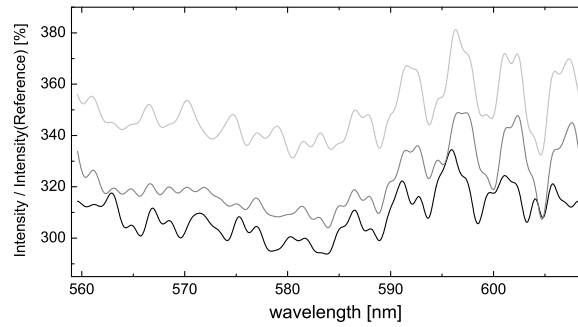
Figure 1: Spectra of a solid AN particle taken at T=293 K, exposure time was 30s. These spectra are taken at the beginning of the experiment (t=2 minutes, black curve), at t=172 minutes (gray curve), and at t=174 minutes (light gray curve).

2-dimensional angular scattering pattern show the same basic features, namely a complex pattern, similar to what has been observed with natural aerosol particles [2], and a significant change in intensity over time periods of seconds. To make a size change of the evaporating non-spherical particle visible in its resonance spectra, we proceed as shown in Fig. 2. Here, panel (a) shows a times series of raw spectra (gray scale intensity coded), with a 120 seconds time lag between consecutive spectra. Clearly, what is most apparent is the change in total intensity from spectrum to spectrum. Most likely, rotational Brownian motion does not lead to a complete orientational averaging within the exposure time of 30 s, and hence the irregular morphology causes the integrated intensity to fluctuate. To eliminate this intensity fluctuations, each single spectrum is separately normalized to its own maximum and minimum of intensity and the result is plotted in panel (b). The most prominent features here are intensity extrema at certain wavelength (roughly regularly spaced) which are not time dependent. Further normalization is
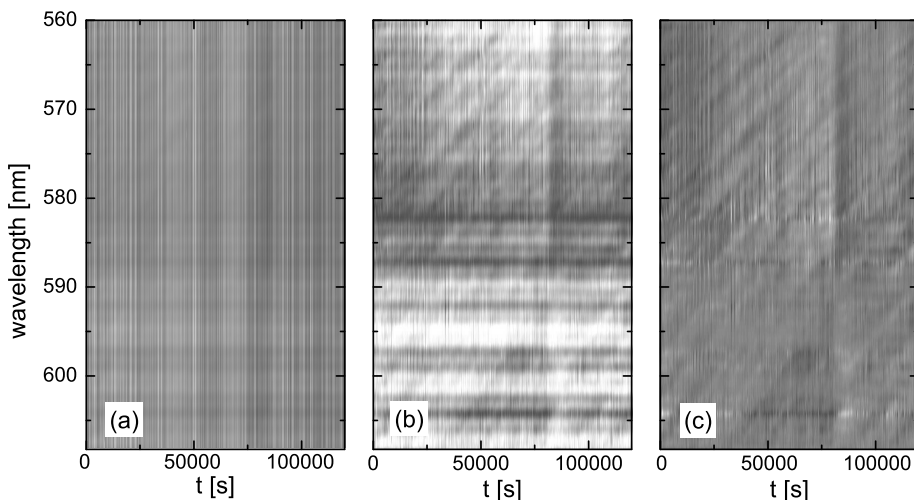

Figure 2: Panel (a) shows the raw spectra of an AN solid particle versus time (wavelength on vertical axis, b/w coded intensity). The intensity of each spectrum are normalized to the same maxima and minima in panel (b). In panel (c) the data of panel (b) are normalized with the mean spectrum of the complete time series.

performed in panel (c) by dividing each spectrum by the mean spectrum of the complete times series. Thus, the non time dependent features are suppressed and intensity bands shifting with time become visible, although not nearly as distinct as in the case of an evaporating liquid, i.e. spherical, particle [1]. Now we assign to such a band a specific size parameter x_0. If we assume the spacing of the bands in wavelength to correspond to that of a Mie-sphere of the same size, we can estimate the initial radius, and follow the temporal evolution of the radius by measuring the wavelength, $\lambda(t)$, of the chosen band at each time which yields then $r(t) = x_0/2\pi\lambda(t)$ [1].

It is difficult to assess the validity of these assumptions from light scattering theory, because we do not know the exact morphology of our effloresced non-spherical particles and an exact treatment would be computationally expensive for a very complex morphology. However, there is indication that effloresced particles are best described as perturbed spheres [2]. To test whether the basic features of Fig. 2 can be reproduced by a simple model of a perturbed sphere, we used the T matrix code of Mackowski and Mishchenko [3] to calculate the random-orientation backscattering intensity of a cluster of spheres shown in Fig. 3, panel (a). Here, we assume that a large sphere at the core does not change its size during evaporation but just a "layer" of small spheres covering the surface of the large sphere. The total radius of the cluster is 2.14 μm for the first simulation decreasing to 1.32 μm with a step size of 0.02 μm. The result of the simulation is very encouraging by showing the same kind of pattern in panel (c) as was observed in the experiments. If we apply the same analysis as for the experimental data to deduce the temporal evolution of the radius, we obtain a radius rate of 0.0274 μm/step, which is 37% higher than the input step size, but still very close. Also, we note that it would be computationally very expensive to perform simulations for the size parameter range of our experimental particles with a more realistic morphology, i.e. more smaller spheres attached to the surface of the inner core sphere. But despite these limitations, we feel that the simulations are reproducing the observations remarkably well, justifying our procedure to evaluate the radius rate.

In order to determine the vapor pressure from the radius change, the following considerations must be taken into account. A solid (or aqueous) evaporating AN particle dissociates in ammonia and nitric acid in the gas phase through the reaction: $NH_4NO_3(s) \rightleftharpoons NH_3(g) + HNO_3(g)$,
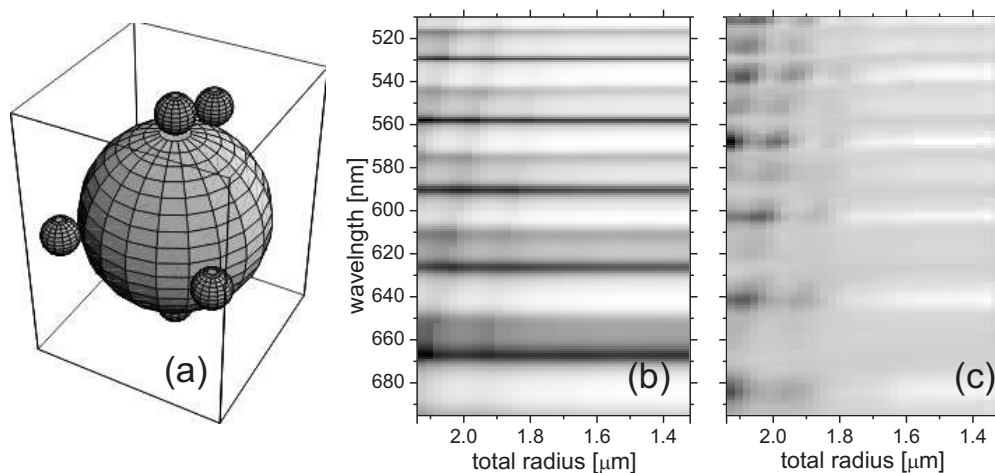

Figure 3: Panel (a) shows the geometry of our simplified model for a perturbed sphere. It consists of a sphere of 1.2 μm radius in the center with 6 attached spheres of smaller radius, decreasing from 0.47 μm to 0.06 μm in radius during the simulation. Panel (b) shows a series of the corresponding simulated spectra with the backscatter intensity gray scale coded. Panel (c) shows the spectra normalized with the mean spectrum of all the simulations, comparable to panel (c) of Fig. 2.

which yields the total pressure in the gas phase as:

$$p_{tot} = p_{NH_3} + p_{HNO_3} = -\frac{1}{2}\frac{dr^2}{dt}RT\frac{\rho_{AN}}{M_{AN}}\left(\frac{1}{D_{NH_3}} + \frac{1}{D_{HNO_3}}\right),\tag{1}$$

where R is the ideal gas constant, T the ambient temperature, ρ_{AN} and M_{AN} the density and molar mass of AN, and D the diffusivities of the two species in the ambient air [1]. We repeated the same experiment as shown in Fig. 2 for different temperatures and a clear temperature dependence of the rate of shift of the intensity bands was evident. The resulting vapor pressures are shown in Fig. 4 together with data from literature. The literature data are extrapolated to lower temperatures in order to compare to our data; the agreement is excellent, but shows also that the enthalpy of evaporation is slightly temperature dependent. **Acknowledgments**:
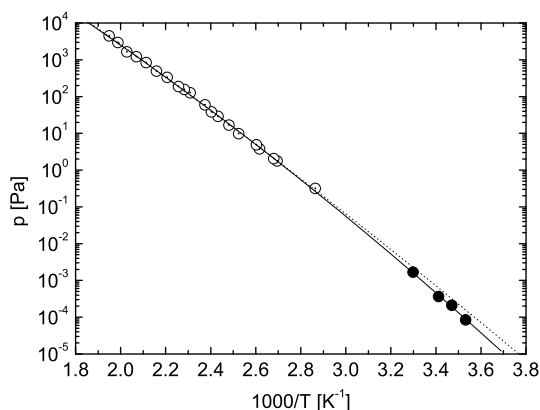
Figure 4: Vapor pressure of a solid AN particle versus inverse temperature. Solid circles: this study; open circles: Brandner et al.[4]; dotted line: extrapolation of the Brandner data to low temperatures; solid line: polynomial 2 nd order fit to all data points.

References

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