**Atmospheric
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Interactive
Comment

Interactive comment on "Optical properties of absorbing and non-absorbing aerosols retrieved by cavity ring down (CRD) spectroscopy" *by* A. A. Riziq et al.

A. A. Riziq et al.

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We appreciate the comments raised by the three referees. Below please find a detailed account of our reply to each one of the those comments. Changes in the text were added accordingly.

Responses to referee #1 (S.S. Brown):

1) Despite the fact the equation 3 and 4 appeared already in the literature, we think that it is necessary to present them here again for readers that are exposed to this type of experiments for the first time. With regards to Equation 5 we added the text as requested.

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2) In a previous setup that we used we had single input and output lines. In that setup there were large variations in the extinction cross section measurements. These variations were minimized in the current setup (4 input and output lines). By increasing the number of input and output lines, it is expected that the flow velocity variation between the incoming and outgoing lines and inside the cavity is minimized. As a result we obtain better mixing and a more homogenous flow inside the cavity (iso-kinetic transition effect). Regarding the loss inside the cavity, we examined this issue carefully by measuring with the CPC the concentration of the particles before and after the cavity and found $> 98\%$ identical concentrations, as described in the paper.

3) We accept the referee point of view of unavoidable multiple modes in pulsed cavity ring-down. This is a well-known issue. However, using a spatial filter as described in the paper reduced the effect of multiple modes substantially, and as mentioned in the comment, we always optimize the shape of the exponent and try to improve it to a single decay. We also noticed that using a tight focusing lens improves the shape of the exponential decay (the lens has a focal length of 5 cm, and the position of the lens is critical for optimizing the decay). The photomultiplier was positioned beyond the focal point of the lens, but where the bean that falls on the surface of the photomultiplier was still focused compared to its size when it exits the cavity. Regarding the 16 μsec decay time observed for an empty cavity, we noticed that it is not consistent with the specified reflectivity (99.995%), and that it should be around 67 μsec. However, in recent experiments in which the flow of the dry nitrogen in front of the mirrors is considerably higher and the dilution effect it taken into account (the mirrors were better cleaned), we measured a 60 μsec decay time which is reasonable. It is noted that in the experiments we also care about the single exponential decay, rather than the absolute decay time because we always take the difference in the decay time of the empty and the filled cavity to calculate the extinction coefficient. Finally the energy of the input beam was 0.5-1 mJ. This is now corrected in the paper. The output from the laser was substantially higher than that. However, the use of irises and the spatial filter reduces the energy of the beam at the input of the cavity to 0.5-1 mJ.

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4) As the reviewer suggests, we added to the parenthetical comment, "Ě(taken as the standard deviation of repeated measurements of the same particle size but for different concentrations)." Earlier in the same sentence, we also added, "Ě'merit function' (similar to a variance).

6) Recently we carried out calculations for the error of the real and imaginary parts of the refractive index (details of the calculations and the exact value of the error will be described in a further publication). In these calculations we checked what would be the resulting error by mapping out the phase space of n and k. The estimated error for the real part of the refractive index with the method that we used for calculating the error is in the order of 10-3 in most of the cases which suggest using the precision of 4 significant figures. In the case of pure Rh-590, the error is ~20% as can be noticed from the poor fit of Mie curve (see Table 4). Therefore, we corrected the precision of the real part of the refractive index of Rh-590 to 2 significant digits. In the case of the imaginary part of the refractive index the error justifies 3 significant digits for all the cases.

7) The sentence was omitted.

8) The value of the retrieved refractive index is now added to the tables.

9) Typographical errors were all fixed

Responses to referee #3

1) A text describing the mixing rules is now added to the Introduction of teh paper.

2) For the mixed particles, in cases where the components dissolved very well (as in the case of glutaric acid and sodium chloride), we assume that the mixtures are homogenous since even when water evaporates from these aerosols, there is still a possible interaction between the sodium chloride and the carboxylic sides of the glutaric acid. This is also supported by the good agreement with the mixing rules results. For mixtures of materials that are not well dissolved in water, the solid mixture may in principle be inhomogeneous. That in principle may affect the scattering and absorption

properties of the aerosols. We cannot rule out the possibility that this is the case for the mixture of Rhodamine 590 with ammonium sulphate. To minimize this, we added methanol to improve the solubility of Rhodamine 590 in this mixtures. Based on the fits and agreement with the mixing rules calculations, we believe that if it is a problem - it is only in the mixture that contains the highest Rhodamine concentration.

3) Figure 7 was corrected.

Responses to referee #4

GC1. The dispersion from the monodisperse aerosol population wasn't taken into account in performing the Mie fitting curve; however, this dispersion is very small (5-7%) for small particles (150nm-650nm). Since we only worked with such small particles, we did not take this into account in our calculations of the Mie fitting curve. The good agreement with literature values for various aerosol types (including new measurements we performed with an absorbing aerosol - nigrosin - not shown in this paper) also suggests that this source of error is not large.

GC2. We agree with the referee's point of view that the ring down for particles would have a larger fluctuation compared to that of the molecular absorption case due to the variations in the concentration of particles inside the cavity. In fact, our calculation was done for the cavity filled with nitrogen and therefore this sensitivity would be the instrumental limit. Since the scope of this paper is not to deal with the statistical fluctuation, we didn't perform this type of calculation. However, Pettersson et. al. (Journal of Aerosol Science, 35 (2004) 995-1011) treated this type of error in detail. According to their calculation, the sensitivity of the system, taking into account fluctuations in the aerosol concentration, remains on the same order of the instrumental limit. Our system has similar parameters to that of Pettersson et al, hence we expect that the error will also be on the same order as the one we quote. In our revised manuscript, we explore this issue further and cite Pettersson et al..

GC3. The error bars of the extinction were deduced by measuring the extinction of

specific size of the aerosol at a specific concentration, and then repeating the measurement at different concentrations of the aerosol using the dilution apparatus described in the article. This procedure was repeated several times (4-7) and the standard deviation of extinction cross section and the extinction efficiency were taken from these measurements. This is now clearly stated after equation 11.

GC4. The reason for using a subset of the data for performing the Mie fit is that (larger) multiply-charged particles contribute more to the extinction compared with particles of small sizes. As explained in the article, this effect was reduced by shifting the distribution of the particles as we examine the different sizes by adjusting the dilution of the solution. For large particles (above 350nm) this effect become negligible since the number of doubly charged (which have the strongest effect) is lower. However, for the smaller particles, it becomes more difficult to shift the distribution because an enormous dilution is required for reducing the doubly charged particles. The experiments with NaCl and glutaric acid (and their mixtures) were done as the latest stage. In these experiments we used the highest dilution (from 0.5gr/100ml to about 20mg/100ml) and this substantially shifted the distribution (peak around 150 nm). This certainly helped in reducing (even overcoming) the multiply charged particles issue and therefore these results are the best in this respect (and the merit functions in this case for both the 350 nm subset sizes and all the sizes are very close). In general, what we propose in this paper is consistent in the way that reducing the effect of multi-charged particles reduces the merit function. In a set of separate, yet unpublished results, we worked with three different concentration ranges to cover the entire 175nm and 475nm size range: the most dilute solution was used to study 175-275nm particles, a second solution for the 300 to 375nm range, and the most concentrated solution for the 400 to 475 nm range.

SC1. Corrected

SC3. The statement was changed as the reviewer suggests.

SC4. The figure includes now the fit for all particle sizes.

SC5. We calculated using the mixing rules described in the paper to check the contribution of possible methanol to the refractive index. The error in the absorption component of refractive index of a mixture of 1% methanol (assuming that 10% of the original 10% mixture remains in the aerosol) with 99% of an absorber (R-590) is 1%. For the real part it is 0.3%. We added the following statement to the text, "Because methanol is a fairly optically neutral substance (with real index close to that of water - between that of ammonium sulphate and Rh590 - and zero imaginary index), the possibility of a slight amount of methanol remaining in the aerosol is not likely to have altered the total extinction coefficient of the mixed aerosols by a measurable amount."

SC6. The statement was removed.

SC7. This was corrected. (Scaling the figure of the residuals)

SC8. The extra sentience was removed

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 12347, 2006.

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