Experiments on neutral cluster generation and detection below 2 nm size

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The research of atmospheric nucleation has gone down to sizes of individual molecules and molecular clusters which have led to development of new instruments capable of detecting single molecules and clusters down to 1 nm. Airmodus particle size magnifier (PSM, Vanhanen et al 2011) has been successfully applied to chamber and ambient measurements (Kulmala et al. 2013, Kirkby et al. 2011), however, to convert the signal of the instrument to absolute cluster and particle concentrations remains extremely difficult due to the varying response of the PSM to ions of different chemical composition and sample carrier gas conditions as we have shown in our previous study (Kangasluoma et al. 2013). In addition to this, one not answered and studied question due to its difficulty is: what is the PSM response to neutral clusters in the sub 2 nm sizes?

To study this problem we utilized the aerosol generation method used in Kangasluoma et al. (2013). Briefly, ammonium sulphate is evaporated to grade 5.0 cryo nitrogen, cooled down to prevent growth, charged with a ^{241}Am source and finally the sample is size classified with Herrmann type high resolution differential mobility analyzer (Herrmann et al. 2000). After size classification, we neutralized the negatively charged aerosol by transporting positive charger ions to the sample flow with an electric field against a flow of nitrogen. Measuring the sample then by mass spectrometer or another DMA, a quite constant neutralization efficiency of about 18 % was observed. The fact that ion-ion collisions occurred was expected, but the question, what the neutralized sample was remains open.

To get the first hints what happened in the collision, we used the PSM as detector with varying detection efficiency. In contrary to normal PSM operation mode we altered the saturator temperature instead of the saturator flow to keep the flow dynamics constant. Electrometer was also used in parallel with the PSM to monitor that the total concentration stayed constant, and we tested that the PSM did not detect the ions pushed to the sample flow even with the highest detection efficiency.

The results are presented in figure 1. Blue dots represent the detection efficiency of the "normal" negative ammonium sulphate with diameter of 1.7 nm and the data is normalized to reach unity as the detection did not increase in the highest saturator temperatures. The rest of the data is scaled with the same factor. When the neutralizer is switched on, the PSM detects negative clusters plus the neutral clusters (Ne+N). This is shown by red dots. It is immediately seen that with lower detection efficiency the PSM detects less Ne+N than completely charged sample. When the temperature is increased, the PSM detects the opposite: more Ne+N than completely charged. With charger on and ion filter at the PSM inlet we measured only the completely neutral sample which is given by black dots. This was to verify that we actually generate neutral clusters. By assuming that 18 % of the charged aerosol is neutralized (multiplying electrometer concentration by 0.18 and comparing that to neutral concentration), we get the green dots which show that when the PSM detection efficiency is increased enough, all neutralized sample is detected as double counts. In other experiments we found that by still further increasing the detection efficiency, neutralized clusters might be detected as triple counts. So far we are not able to explain the results in any other way than that the ion-ion collision breaks the charged ammonium sulphate cluster apart and both, or all, resulting neutral clusters are observed when PSM detection efficiency is increased. As we have no method to characterize the neutral clusters, we cannot conclude anything about the detection efficiency of the neutrals compared to the charged clusters. This study however shows that ion-ion collision might lead to something else than recombination and is under further study. Ultimately the objective of these studies is to give complete detection efficiency curve for neutral cluster detection of the PSM.

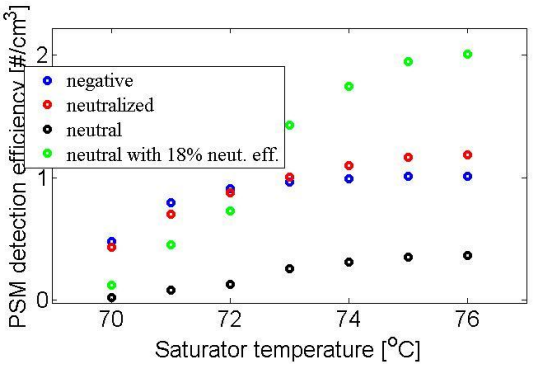

Figure 1. Scaled PSM detection efficiencies as a function of saturator temperature for negative 1.7 nm ammonium sulphate. Explanation of the data is given in the text.

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