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Water uptake impedance of glassy organic aerosols

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Depending on their concentration and composition, aerosols affect various atmospheric properties and processes, such as atmospheric chemistry and Earth's radiative budget. The atmospheric aerosol itself is a complex mixture of various inorganic and organic components, whereas the organic fraction can represent more than 50% of the total aerosol mass. It was recently shown that aerosols high in organics may be present in a glassy state (Zobrist et al., ACP, 8, 5221-5244, 2008). The glassy nature of the aerosols may influence their properties and restrict their functionalities severely, e.g. their water uptake, heterogeneous chemical reactions in their bulk or on their surfaces, as well as ice nucleation and ice crystal growth.

Here, we present the first experiments on the water uptake by single levitated glassy aerosol particles using an electrodynamic balance (EDB). Sucrose was chosen as a model substance, which comprises functional groups typical of organic species in the atmosphere. In addition we developed a microphysical model, which enables us to calculate the liquid diffusion inside a glassy particle using water diffusion coefficients in aqueous sucrose particles adapted from the literature. As the diffusion coefficient of water in the particle, D(cH2O), depends on the water concentration cH2O itself, the solution of the diffusion equation presents an interesting non-linear problem. The combined experimental and modelling approach allows describing in detail the water uptake by glassy aerosols at atmospherically relevant temperatures and relative humidities (RH).

Hygroscopicity cycles were perfomed in the EDB starting from a crystalline (non-spherical) sucrose particle at 291 K. No water uptake was observed while RH was increased until the particle deliquesces at roughly 85% RH leading to a liquid (spherical) particle. In the subsequent drying cycle, surprisingly no efflorescence was observed when the particle was dried to below 5% and it remained spherical. The particle was then investigated in a second humidifying cycle. This time, the particle started to take up water already at ∼40-45% RH. At higher RH (>55%), the particles turned liquid again, agreeing well with the previous cycle. The Differential Scanning Calorimeter (DSC) experiments of Zobrist et al. (2008) show that a sucrose particle is in a glassy state below 30% at 291 K. Thus we conclude from the DSC result together with the perfect sphericity of the particle at low RH that it was in a glassy state when the second humidifying cycle was started. This indicates that a glass-to-liquid transition can occur in particles with atmospherically compositions and sizes, without requiring a change in temperature. Furthermore, it is evident that the glass curve estimated with the DSC by Zobrist et al. provides only a lower limit, and that water uptake is further delayed in the temperature/humidity range just above glass point. This indicates that the water diffusion coefficient, D(cH2O), is the key parameter in these experiments. Similar hygroscopicity cycles with sucrose particles have also been performed at 254 K and 272 K, confirming the above conclusions. - In a second set of experiments, we tried to quantify D(cH2O) at low RH for glassy sucrose particles. This time the hygroscopicity cycle was stopped at roughly 10% RH below the water uptake observed in the previous experiments and thus RH was kept constant at roughly 35% for a few days. It was found that the radius of the particle very slowly increased although RH and the temperature were kept constant (T = 272 K). Preliminary estimates suggest D(cH2O) ∼ 10**-19...10**-20 m2/s at these conditions, indicating that a glassy particle with a radius of 50 nm would need roughly 8 to 80 hours to turn into a liquid. This is a timescale important for atmospheric considerations.

The microphysical model confirms the results of EDB experiments, revealing a significant impedance of the water uptake by organic aerosol particles at temperatures important for cirrus clouds formation, and hence a potential clue on how to solve the recently discussed upper tropospheric "supersaturation puzzle".