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Quantifying water diffusion in secondary organic material

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Recent research suggests that some secondary organic aerosol (SOA) is highly viscous under certain atmospheric conditions. This may have important consequences for equilibration timescales, SOA growth, heterogeneous chemistry and ice nucleation. In order to quantify these effects, knowledge of the diffusion coefficients of relevant gas species within aerosol particles is vital.

In this work, a Raman isotope tracer method is used to quantify water diffusion coefficients over a range of atmospherically relevant humidity and temperature conditions. D_2O is observed as it diffuses from the gas phase into a disk of aqueous solution, without the disk changing in size or viscosity. An analytical solution of Fick's second law is then used with a fitting procedure to determine water diffusion coefficients in reference materials for method validation. The technique is then extended to compounds of atmospheric relevance and α-pinene secondary organic material.

We produce water diffusion coefficients from 20 to 80 % RH at 23.5˚C for sucrose, levoglucosan, M5AS and $MgSO_4$. For levoglucosan we show that under conditions where a particle bounces, water diffusion in aqueous solutions can be fast (a fraction of a second for a 100 nm radius). For sucrose solutions, we also show that the Stokes-Einstein relation breaks down at high viscosity and cannot be used to predict water diffusion timescales with accuracy.

In addition, we also quantify water diffusion coefficients in α-pinene SOM from 20-80% RH and over temperatures from 6 to -30˚C. Our results suggest that, at 6˚C, water diffusion in α-pinene SOA is not kinetically limited on the second timescale, even at 20% RH. As temperatures decrease, however, diffusion slows and may become an increasingly limiting factor for atmospheric processes. A parameterization for the diffusion coefficient of water in α-pinene secondary organic material, as a function of relative humidity and temperature, is presented. The implications for atmospheric processes such as ice nucleation and heterogeneous chemistry in the mid- and upper-troposphere will be discussed.