First Steps in Atmospheric Particle Formation

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We present here the results of combined experimental and molecular dynamics (MD) computational study of pickup of atmospheric molecules on water nanoparticles (clusters). These could be viewed as the precursors for the larger atmospheric particles – aerosols and ices.

First we focused on adsorption of H_2O, NO, and NO_2 molecules on large pure water clusters. Clusters with mean size 260 or 430 water molecules were prepared in the water vapor expansion into the vacuum. Skimmed beam passed through pickup chamber, where the gas of interest was introduced. After pickup the cluster speed distribution was measured using pseudorandom chopper technique. The pickup cross section was then estimated on the basis of the speed variation with the pickup cell pressure. Details can be found in current publication Lengyel *et al.* (2012). Fig. 1 represents the comparison between measured cross section and geometrical cross section for cluster. We can see that cross section for water adsorption is more than 2 times the expected value.

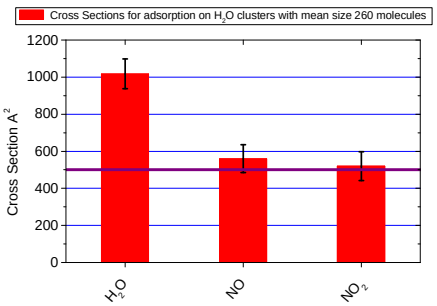

Figure 1. *Comparison of measured sticking cross section values with geometrical cross section (purple line).*

Except the particle growth, adsorption on ice particles is important prerequisite of heterogeneous chemistry in atmospheres. Independent of the reaction, the most important step is the reactant adsorption on the particle. Cross section is than fundamental characteristics of the adsorption process. In present study it was measured for several species relevant for atmospheric chemistry, mainly halocarbons, but also HCl, HBr, methane or alcohols. All show significant divergence from the geometrical cross section predictions.

We employ MD simulations to understand the observation. At first MD simulations were used to confirm the suitability of the experimental method. The most important assumption during the estimation of adsorption cross section is that only sticking collisions lead to nonstochastic momentum transfer between cluster and gas in the pickup cell. Demonstration of this fact can be seen on Fig. 2. Additionally, by fitting the step function like showed on Fig.2 to the data from MD simulation we estimated sticking cross section values in good agreement with experiment. Supported by agreement we try to illuminate the physical processes behind the CS discrepancies. Fitting the MD model interaction potential between the cluster and impacting molecule we obtained r^{-3} potential dependence. The long range potential can lead to significantly higher cross section in comparison to Van der Waals interaction r^{-6}, which is usually neglected.

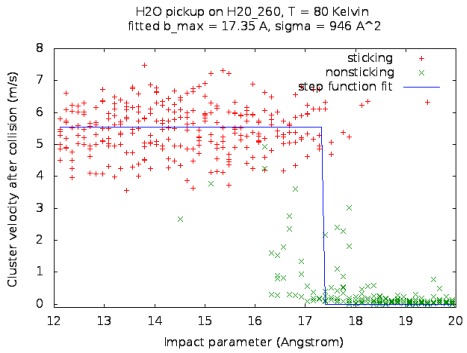

Figure 2. *Effect of sticking + and nonsticking x collisions on the change in the cluster velocity after collision, together with step function fit modelling the measured cross section value.*

The study shows that the formation of PSCs can be significantly faster than expected. Also the sticking probability of various heterogeneous chemistry precursors differ significantly from the expected values, what can have impact on the future ozone level predictions. More important it shows us that neutral-neutral interaction in the case of large particles can have long range character and needs more detailed exploration.

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