

New experimental tools for characterization of nucleation and reactivity in small aerosols

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Keywords: nitric acid, solvated electron, mass spectrometry, nucleation.

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The study of atmospheric aerosols attracts a considerable attention because of its influence on atmospheric chemistry and climate. Perhaps the most famous example is the ozone hole where the polar stratospheric clouds play a key role in the ozone depletion process (Finlayson-Pitts and Pitts, 2000). The atmospheric aerosol particle generation starts with growing of small aerosols and ice nanoparticles via nucleation and uptake of various atmospheric molecules on these particles. Therefore the uptake processes have recently been investigated in our laboratory (Lengyel, Kočišek *et al.*, 2012). The dissolution of water with hygroscopic species such as H_2SO_4 and HNO_3 substantially speeds up the aggregation leading to the homogeneous heteromolecular nucleation of clouds in troposphere and stratosphere.

There are several experimental methods based on mass spectrometric techniques that can provide comprehensive information on the chemical composition, size, morphology and phase of aerosols (Laskin *et al.*, 2012, Kolb and Worsnop, 2012). In the presented work, the nucleation of mixed nitric acid/water aerosols is investigated by two different mass spectrometric techniques providing complementary information. In both experiments the small aerosol particles were produced by supersonic expansion of saturated nitric acid vapor seeded in buffer gas, and mass spectra were investigated by a reflectron time of flight mass spectrometer. The aerosols were ionized by electrons in one case, while sodium doping followed by UV photoionization was implemented in the other experiment.

This unique combination of both techniques (shown in fig. 1) reveals that only aerosols containing at least one acid molecule are generated, i.e. the acid molecule serves as the nucleation centre in the expansion. The experiments also suggest that at least four water molecules are needed for HNO_3 acidic dissociation. The small aerosols are undoubtedly generated, as proved by electron ionization; however, they are not detected by the Na doping due to a fast charge-transfer reaction between the Na atom and HNO_3 . It was also confirmed by the *ab initio* calculations. These points to limitations of the Na doping recently advocated as a general method for atmospheric aerosol detection. On the other hand, the combination of the two methods introduces a tool for detecting molecules with sizable electron affinity in aerosols (Lengyel, Pysanenko *et al.*, 2012).

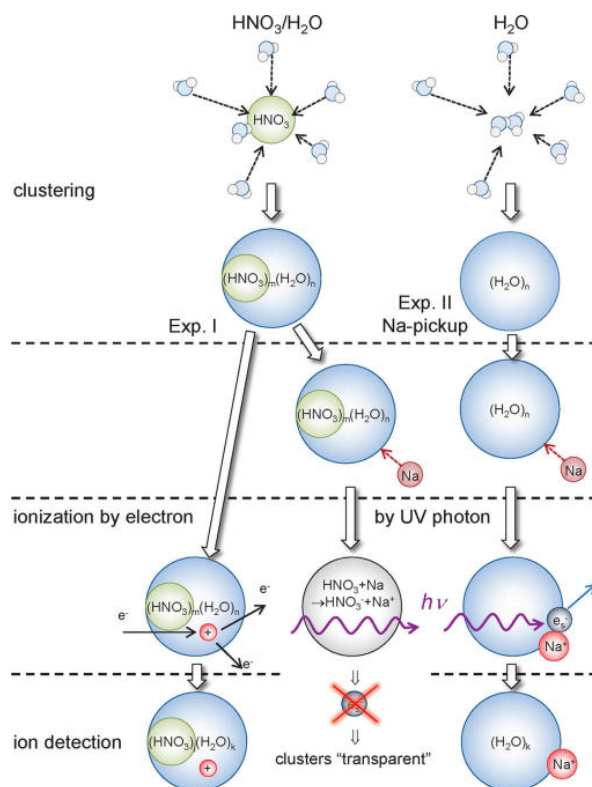


Figure 1. Schematic illustration of processes observed in the present aerosol experiments

This work was supported by the Grant Agency of the Czech Republic under grants P208/11/0161 and 203/09/0422.

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