

# Aerosol particles in molecular beams: pickup of molecules, chemistry and photochemistry

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A unique versatile molecular beam CLUB (CLUstr Beam) apparatus has recently been exploited for various studies of atmospherically relevant aerosol particles in vacuum. These studies will be briefly reviewed demonstrating the significant potential which the implementation of the molecular beam techniques has for the aerosol studies.

In molecular beams clusters are prepared by expansion of suitable gases into the vacuum through supersonic nozzles. Depending on the expansion conditions the clusters of various sizes can be generated ranging from a few molecules to small aerosol particles with sizes in the nanometer range composed of hundreds of molecules. Our CLUB apparatus enables various experiments with these particles: (1) doping them with different molecules; (2) investigating photodissociation and photochemistry in/on the clusters by the fragment velocity imaging method; (3) studying the composition, dynamics and reactions by a unique reflectron time-of-flight mass spectrometer.

Several experiments will illustrate the variety of information about the small aerosol particles gained with the CLUB apparatus. First, we will exemplify the pickup cross sections of small ice nanoparticles for uptake of various atmospheric molecules (Lengyel, Kočišek *et al.*, 2012). The cross sections were measured by precise velocity measurements of particles after their passage through a pickup cell filled with the particular gas. The cluster velocity change in dependence on the pickup pressure allows the pickup cross section determination. The experimental results are in good agreement with molecular dynamics simulations. They show that the actual cross section for the pickup is significantly larger than the geometrical cross section. This effect should be considered in the atmospheric models and nucleation theories.

Photochemistry of ice nanoparticles doped by hydrogen halide molecules HX (X= Cl, Br, I) is highly relevant to the stratospheric ozone depletion process. We have studied HX·(H<sub>2</sub>O)<sub>n</sub>, n= 10<sup>2</sup>-10<sup>3</sup>, clusters under the influence of UV laser radiation at 193 nm and 243 nm. A series of experiments and theoretical calculations (Poterya, 2007) (Poterya, 2011) (Ončák, 2011) revealed that the HX molecule is acidically dissociated on the ice particle and a neutral hydronium radical H<sub>3</sub>O<sup>+</sup> is generated upon the UV excitation. This radical also represents a cluster model for solvated electron.

Most recently we have also investigated the photodissociation of CF<sub>2</sub>Cl<sub>2</sub> molecule in clusters revealing the detailed dynamics of the molecular

dissociation, and Cl-fragment caging and escape from the clusters.

Finally, we have studied mixed nitric acid/water ice nanoparticles in two different mass spectrometric experiments (Lengyel, Pysanenko *et al.*, 2012). The comparison between the electron ionization and photoionization after Na-pickup showed that HNO<sub>3</sub> molecules act as very effective condensation nuclei, and no pure water clusters were generated even from vapors with 100 fold excess of water molecules. Besides, we have demonstrated that the Na doping can be used for detection of species reacting with Na or solvated electron in the aerosols.

In general, all these results are relevant for the ozone depletion process in the stratosphere.

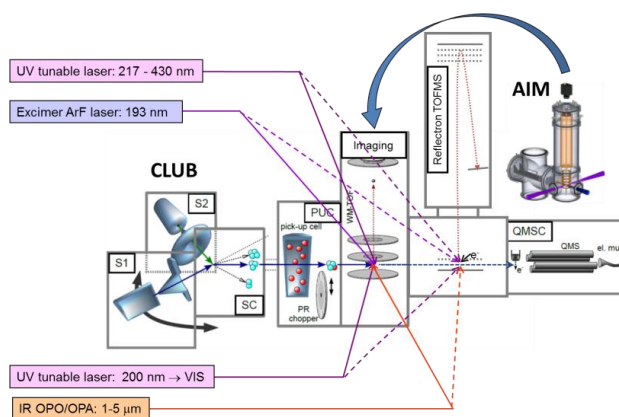


Figure 1. Schematic picture of molecular beam CLUB (CLUstr Beam) apparatus for small aerosol studies.

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