Cluster Measurements at CLOUD using a High Resolution Ion Mobility Spectrometer - Mass Spectrometer Combination

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Abstract. Mass spectrometry is powerful tool for environmental and atmospheric chemistry analysis. Modern mass spectrometers demonstrate low detection limits, high sensitivity, and high resolving power. However, such high performance is not always enough to identify ambient ion clusters due to the clusters braking at the atmospheric pressure-to-vacuum interface of mass spectrometer. This study presents a high resolution ion mobility spectrometer - time-of-flight mass spectrometer (IMS-TOF) in the CLOUD experiment. This combination of orthogonal analytical techniques allows obtaining structural information in addition to mass-to-charge separation.

Keywords: mass spectrometry, ion mobility spectrometry, atmospheric chemistry, CLOUD

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INTRODUCTION

Mass spectrometry (MS) is an analytical technique, which allows identification of ionized particles or molecules by their mass to charge ratios. Since MS discovery, a number of different types of mass analyzers has been invented [1]. However, all of them require keeping the mass analyzer at high vacuum for performing mass separation. Invented later, atmospheric pressure ionization methods (e.g. electrospray, atmospheric pressure chemical ionization) requested a transfer of ionized molecules from ambient pressure to MS vacuum system. This request lead to development of atmospheric pressure interface (API) [2]. Thus, ambient atmospheric ions can be directly analyzed by a mass spectrometer. This is important feature for atmospheric chemistry studies as well.

However, API partly defragments ion clusters and large particles. This complicates of ion clusters identification by mass spectrometer. This issue can be solved by combination of MS and an orthogonal atmospheric pressure analytical method, such as ion mobility spectrometry (IMS). Ion mobility spectrometry (IMS) is a measurement technique where ionized analytes are separated based their mobilities under electric field in flow of neutral gas or air under ambient pressure conditions [3]. A combining IMS together with MS provides a very promising hyphenated technique, especially since mass spectrometry characterizes the ions by mass to charge ratio and therefore allows identification of the ion clusters, which were broken apart in the API [4].

In this work we present preliminary data of clusters analysis by an IMS-TOF, which was first time used in the CLOUD experiment.
**EXPERIMENTAL**

**IMS-TOF**

Figure 1 demonstrates an experimental set-up at the CLOUD. An IMS-TOF (Tofwerk AG, Thun, Switzerland) [5] equipped with a specially designed ion interface was used in this study. The ion interface transfers ambient ions into IMS-TOF by ramping the ions up to potential of IMS-TOF entrance. A corona charger was installed into the sample line of the IMS-TOF for ionizing particles during neutral CLOUD experiments. The IMS-TOF was operated only in negative ion mode.

**RESULTS AND DISCUSSION**

Initial tests of the IMS-TOF demonstrated low transmission of ions through the ion interface in comparison to regular APi-TOF, which was used in the same CLOUD experiment set-up. The IMS-TOF was estimated about 10 times less sensitive. In addition to sensitivity issue, the ion interface discriminates the ionized particles by their mass or mobility. It was admitted, that the ions with higher mass to charge ratio had higher intensities comparing to small ones.

Due to the sensitivity issue a long, up to six hours, spectra averaging procedure was done. Figure 2 shows an example of the six hours averaging of mass-mobility spectra for beam charging run at the CLOUD experiment. Sulfuric acid cluster ions \((H_2SO_4)_xHSO_4^-\) demonstrate the same drift time value. Thus, trimmer cluster ion brakes in atmospheric pressure interface of mass spectrometer to dimmer and monomer ions. However, clusters ions \((H_2SO_4)_xHSO_5^-\) show different drift time in ion mobility spectrometer and this indicates no declustering for those ion clusters.
CONCLUSIONS

The presentation demonstrates first results of clusters measurements in CERN experiment by using of IMS-TOF instrumentation. The IMS-TOF allowed to observe declustering of sulfuric acid clusters at the atmospheric pressure interface of mass spectrometer. This ability also opens a wide range of potential investigations of cluster ions passage through atmospheric pressure interface of API-TOF devices in atmospheric ions measurements. However, the sensitivity issue of reported instrumentation demands further development and improvement of the ion interface.

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REFERENCES