AN INDIGENOUSLY DEVELOPED DUAL TIME OF FLIGHT MASS SPECTROMETER SETUP WITH NANOCLUSTER AND ELECTROSpray SOURCES FOR GAS PHASE STUDIES

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Abstract
This paper reports on the dual time-of-flight mass spectrometer coupled to a magnetron based source for metal nanoclusters and an electrospray ion source for gas phase studies, all developed indigenously. The system consists of a reflectron time-of-flight and a linear time-of-flight mass spectrometers positioned perpendicular to each other. It can distinctly measure time events separated by 1.4 nanoseconds and distinguish species on an abundance scale of 1/2000. Various applications in different studies, e.g. identification of isomers of small water clusters, simultaneous growth of positive, negative and neutral copper clusters and isotopic abundance within single cluster masses are discussed. The studies depict the compatible utility of a sophisticated home-built instrument.

Keywords: Time-of-flight, Nanoclusters, Magnetron, Electrospray, Gas-phase.

Introduction
Understanding the fundamental properties of nanoclusters is indispensable in order to exploit their novel features\textsuperscript{1-3} for technological applications.\textsuperscript{4} Investigations on the intrinsic properties of nanoclusters require an interaction free environment that could be most approximately obtained in gas phase.\textsuperscript{1-3,5} At low density regime the particles here could largely be treated as free giving an advantage to compare the experimental results with calculations\textsuperscript{6-7} done on independent systems. Therefore, studies on free clusters are extremely important and had been the foremost trends in experiment that endeavors to bridge the gap between an atom and the bulk material.

Time of flight (TOF) mass spectrometry is the most advantageous technique for rapid qualitative sampling\textsuperscript{8} of species in gas phase as they typically have a life span in the range of milliseconds. Sophistication in mass spectrometric methods with the advances in technology has made it possible to develop time of flight spectrometers having high resolution, large dynamic-range and sensitivity within the required limits in applications.\textsuperscript{9-14} Through a very wide range of diverse functions, this technique has turned out to be omnipresent in almost every field of science and much superseded to remain as only a tool to measure the mass of an ion. Recent applications are in physical and chemical process studies through sequential sampling over successive duty cycles or else, in tandem MS/MS mode with another TOF or a different type of mass spectrometer. For example, in the measurement of specific heat and thermodynamic properties of metal clusters\textsuperscript{15} and in sequencing studies of amino acids in proteins\textsuperscript{16} etc., the utilization of the technique has been proven to be commendable.

This paper reports on a dual time of flight mass spectrometer coupled to a magnetron based gas-aggregation source for metal clusters and an electrospray ion source for organic
or biological molecules, all developed indigenously using mostly the in-house and/or local facilities. The system has been applied into various studies e.g. addressing the issue of isomers in structural properties of water clusters,\textsuperscript{17} simultaneous growth of positive, negative and neutral metal clusters under one production cycle, isotopic abundance within individual copper clusters etc.\textsuperscript{18} Some of the studies are discussed in short following a brief description of the experimental setup.

**Experimental**

Fig. 1 shows the complete layout of the system. It has three major segments. Segment-1 is the refletron TOF, segment-2 is the linear TOF and segment-3 is the magnetron based gas-aggregation source for metal clusters. The individual internal components of the system are identified within the figure and described at inset-A. Clusters are extracted out of the source through iris and skimmer arrangement c. Ions are injected perpendicularly into the reflectron TOF using ion optics a and coaxial lens l which focus them into the reflectron r for energy compensation and are detected finally in the APTOF detector d. The neutral clusters travel along the zero-degree direction to be photoionized using EXCIMER laser (ArF 193 nm @ 700 µJ per pulse) and rapidly accelerated by applying large opposite potential in between b and the grid g (90%) to inject into the linear TOF 2. Details of the system are published elsewhere.\textsuperscript{9-14,18} The system can distinctly resolve time events separated by 1.4 nanoseconds and its dynamic range can distinguishing species on an abundance scale of 1/2000. Fig. 2 presents the differential pumping arrangements when the electrospray source\textsuperscript{14} is coupled into the system at position n in place of pulsed needle injector as shown in Fig.1. The component e is

![Proportional layout of the complete experimental setup](image-url)
the newly developed Bradbury-Nielsen mass selector\textsuperscript{19} used to segregate single cluster ion of a desired mass for laser photo-evaporation measurements to determine the size specific thermal properties of metal clusters. Fig. 3 shows the model calculation of ion trajectories using SIMION-8 depicting the selection of individual mass out of an ion packet in the cluster beam.

**Results and Discussion**

Fig. 4 shows performance of the electrospray setup through the detection of a commercial dipeptide smaple in methanol solution at 330 picomol/ml concentration and flow rate of 6 μL/mn using 50 μID needle applied to +2700 volts.\textsuperscript{14} The proton added peak is detected with an S/N ratio > 25. Fig. 5 shows different water cluster structures as obtained in calculations.\textsuperscript{6} Fig. 6 shows the data of mixed clusters of water with cyclopentanone done using the technique of gas phase titration.\textsuperscript{17} The conformation of the protonated cluster peaks are levelled in the figure. The ground state isomeric form of 9-19 atom water clusters have been revealed for the first time through an analysis.
of the data. Introducing a concept of relative-coordination, it has been shown that clusters containing more than 20 water molecules are more likely to have open configuration like bond-melted structures obtained in thermal treatment.17

Fig. 7 shows the mass abundance of negatively charged copper clusters obtained using the magnetron based gas-aggregation source 3 shown in Fig.1. Such source has high central axis beam intensity and is demanding for size selective measurements on free clusters. Here,
charging essentially happens through ion-exchange and charge-transfer reactions between an ion or electron with the neutral cluster species. In simultaneous detection, it is seen that negative, positive and neutral clusters occur in 1:2:3 abundance ratio. However, the intensity falls off exponentially for as grown clusters just out of the source as is predicted by many authors and obtained using various other type of cluster sources also. Inset in Fig.6 shows the isotopic abundance within individual 34 atom neutral copper cluster. A maximum of 26 independent Gaussians could be identified. The details of the source and system are published.

Conclusion

This report describes the indigenously built dual time-of-flight mass spectrometer system and its various applications in gas phase studies. The sophistication of this complex system has enabled these studies on involved issues.

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References


