Investigating Inorganic Water Cluster Separation in Differential Mobility Spectrometry

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Introduction

Sample preparation and chromatographic techniques are time-consuming but necessary tasks in the analysis of elemental compounds within complex real-world samples. Such methods are fundamentally limiting for rapid analysis of inorganics in field applications. Differential Mobility Spectrometry (DMS) is a promising alternative to achieve separation of atomic ion clusters on the order of milliseconds.

DMS has been widely implemented into atmospheric pressure inlet mass spectrometers for the separation of primarily organic molecular species. Separation in DMS normally differentiates ion trajectories across three types, A-, B-, and C-type ions as shown in Figure 1. A-type behavior is typically associated with clustering phenomena. Clustering mechanisms may be presumed to dominate from electrospray ionization methods due to residual solvent.

In the work described herein, we present our experimental plans to rigorously investigate the role of water solvation in DMS dispersion of metal ions that we have observed previously.
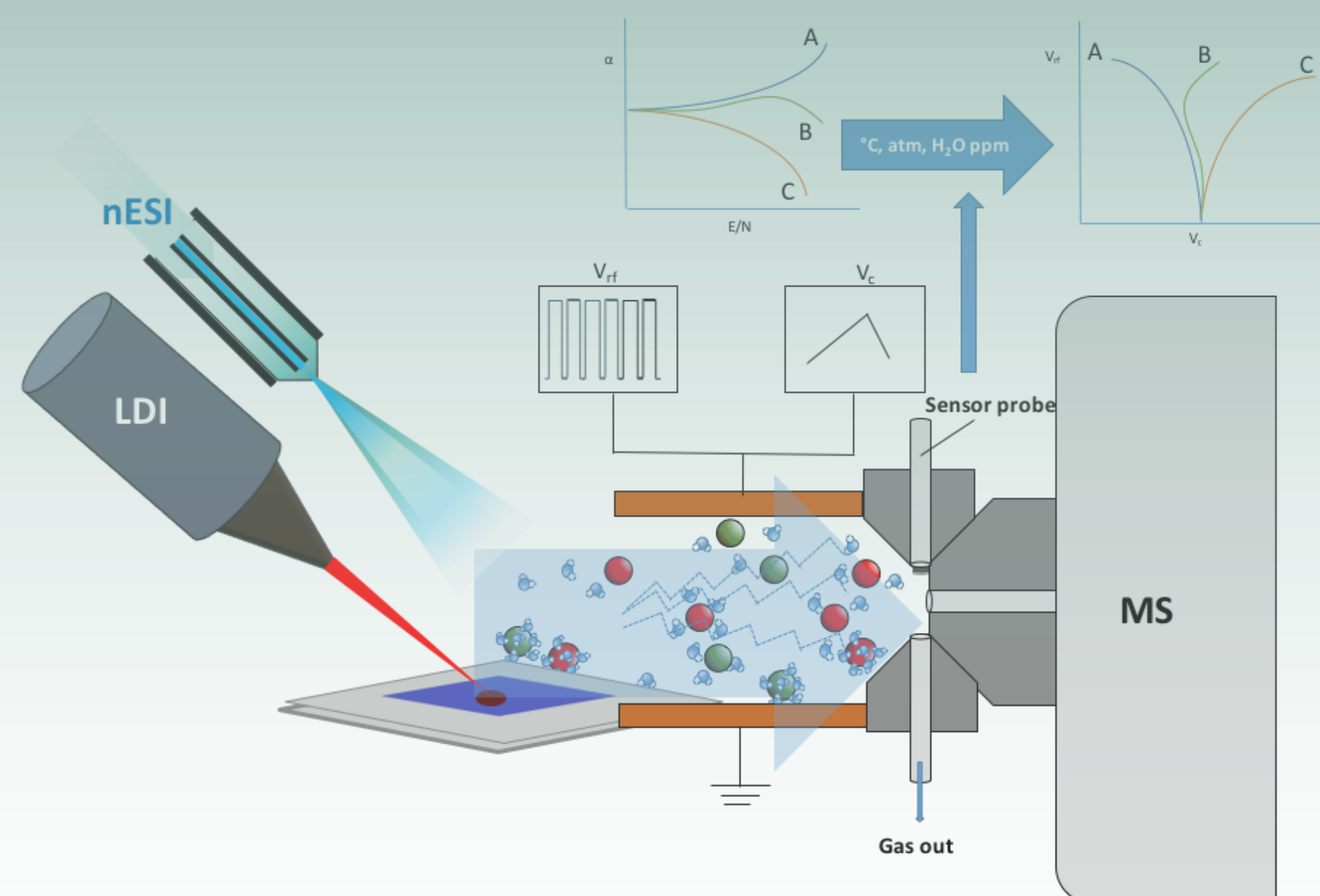

Figure 1. Conceptual design of the experimental set up including the interface of multiple atmospheric pressure ionization sources to DMS-MS.

Hypothetical Separation of Metals

The separation capability of DMS can be described by the "alpha function" which depends on the field strength; which is the *ratio* of E (electric field) to N (gas density):

$$K(E/N) = K(0)[1 + \alpha_2(E/N) + \ldots + \alpha_{2n}(E/N)]^{2n}$$

where $K(0)$ is the coefficient mobility of ions at low ($E = 0$) electric field conditions, and the alpha coefficients: $\alpha_2, \alpha_4, \alpha_6, \ldots, \alpha_{2n}$ are dependent on the E/N usually represented by the Townsend unit (1 Td = 10^{-17} V·cm^2).

We have reported earlier on the feasibility of DMS to pre-filter inorganic ions toward the identification of radionuclide components in nuclear forensic applications.[1] Derivation of the alpha parameter for metal ions from the mobility tables by Ellis et al,[2-3] In Figure 2, we applied he DMS modeled in SIMION; the expanded x-y plane cross-sectional view shows the carrier gas and ion as they travel between the electrodes of the DMS.
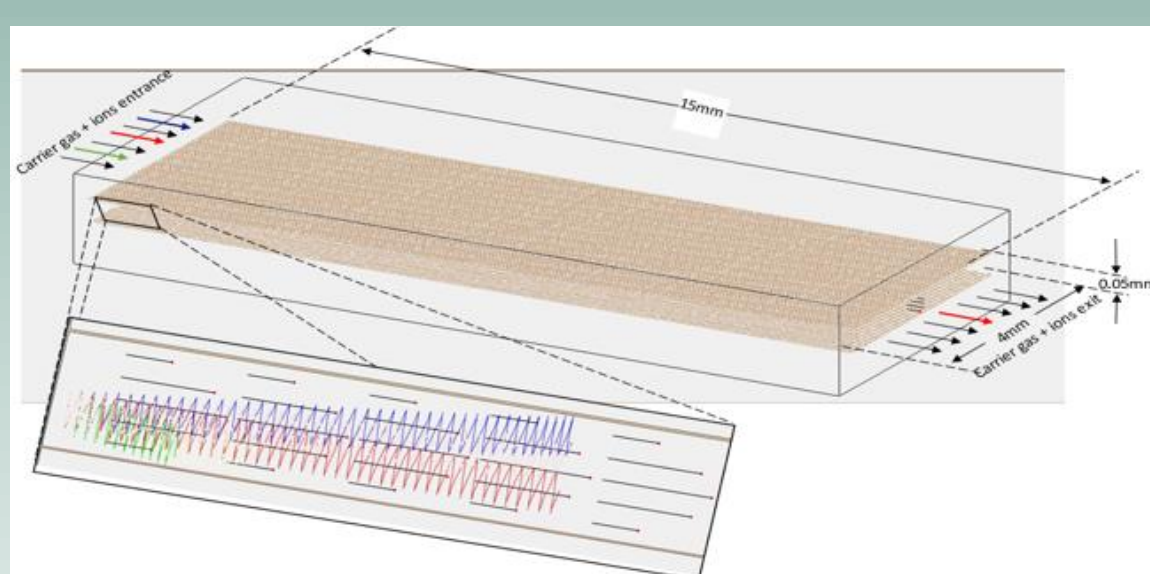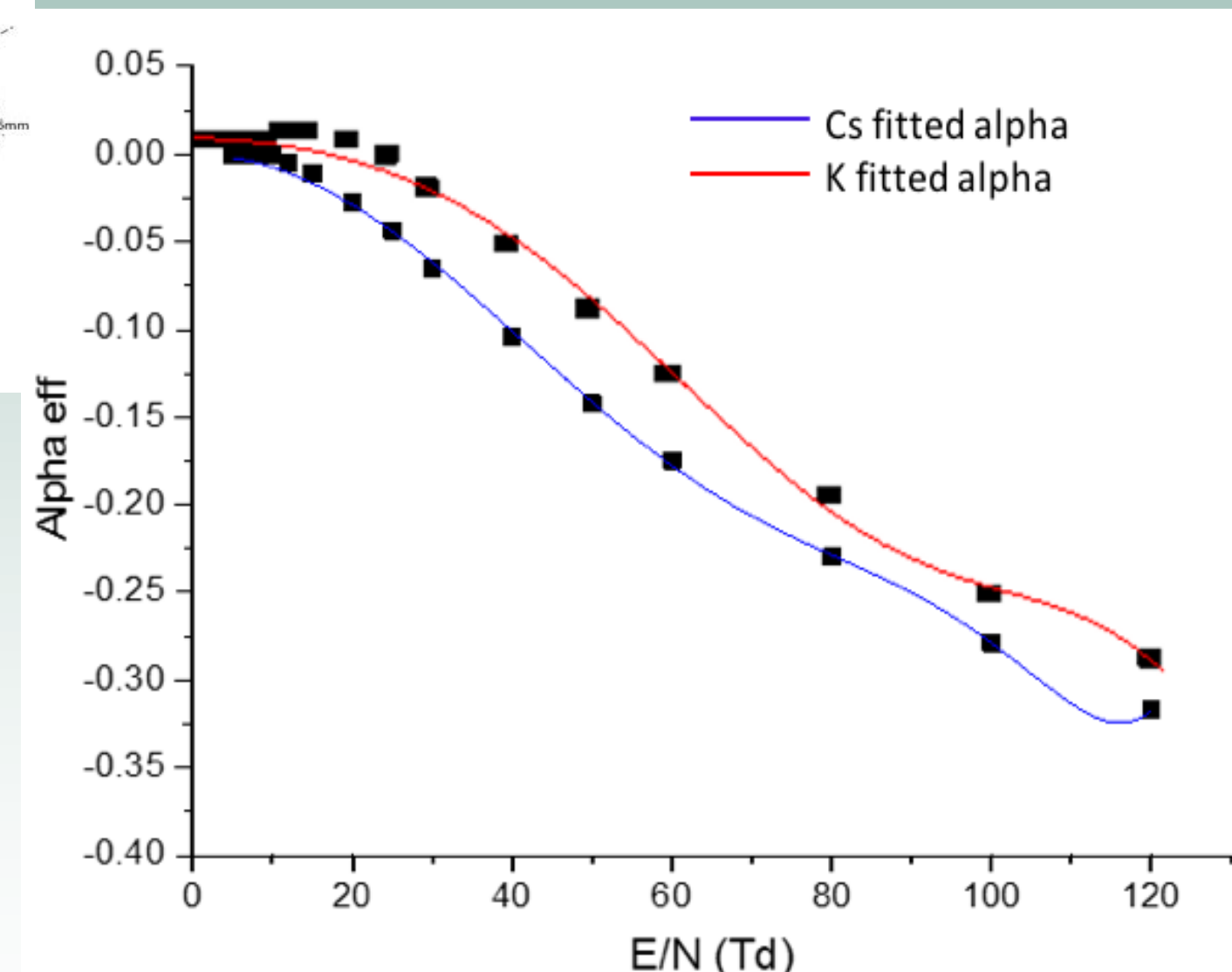

Figure 2. above) SIMION simulations were implemented to demonstrate ion separation through a hypothetical DMS chamber. right) differential ion mobility data was derived from literature measurements experimentally taken across wide electric field conditions by Ellis et al.

Methods

Control of the DMS flow rate is independently maintained through an external pumping chamber positioned between the DMS and the commercial MS (a Thermo LCQ). The interface design must flexibly accommodate the front end home-built DMS cell. We base our initial adaptable DMS design with two stainless steel electrodes within housing fabricated from Vespel. The DMS mounts through a face-mounted o-ring to maintain a leak-tight transmission from the DMS into the interface. The resulting DMS-to-MS interface was designed in Solidworks and fabricated in PVC by the USF Engineering Center's Machining Facilities.

Currently, the driving voltage potentials are supplied to the DMS electrodes by legacy Sionex electronic hardware (Figure 3). The low power electronics achieve V_{rf} up to 1500 V amplitudes using a flyback transformer design. Sionex's Expert software provides control of dispersion (V_{rf}) and compensation (V_c) voltage parameters similar in implementation to chromatographic methods timetables. Ions introduced into the DMS are meant to undergo collisions and reactions to effectively control solvation prior to DMS entry. Additional electronic hardware has been implemented to provide field gradients across these chambers.
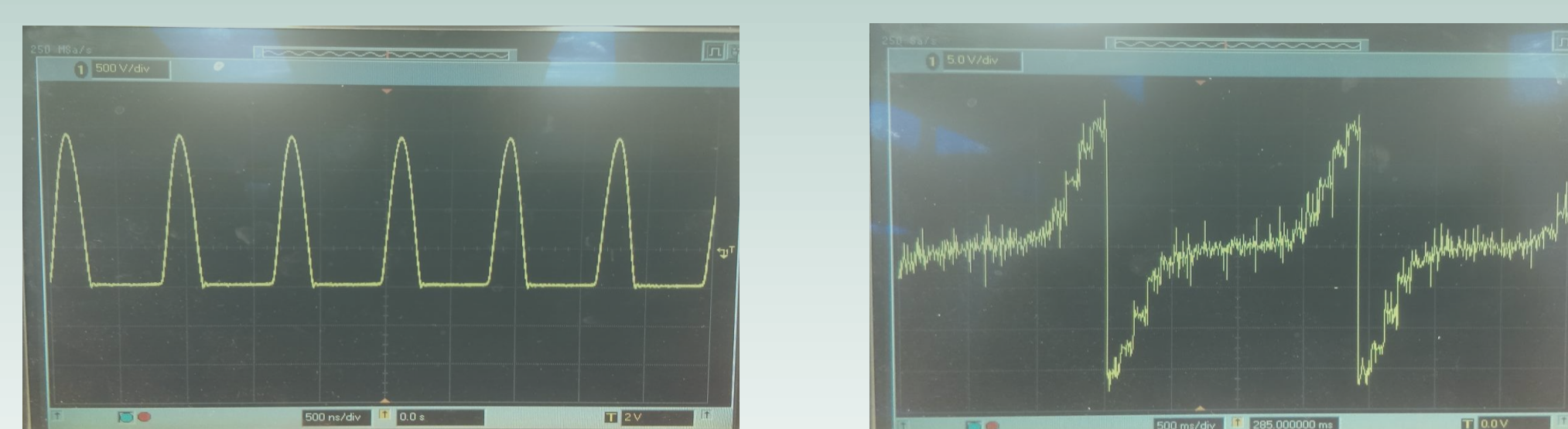

Figure 3. A typical DMS electronics V_{rf} and V_c scan output signals displayed on the oscilloscope. left) V_{rf} = 1500V. right) V_c scan= -15V to +15V

The DMS housing features through a shaft-mounted o-ring assembly to accommodate a potential enclosed reaction chamber, monitored for DMS gas conditions. Ultimately the reaction cell shall interface directly with multiple API sources including both nanospray and laser desorption ionization. We design an optical path to constrain ablation of samples from bare metal standards.

Ambient Laser Ionization

Nanoelectrospray ionized samples can be introduced in an open air configuration ahead of DMS. Dissolved salt samples are supplied to a nESI needle with the help of a syringe pump. However, the specific solvation of ions cannot be easily constrained in this manner though it is likely that control of humidity is critical to achieving reproducibility. Thus we sought to produce minimally solvated ions from a laser ionization configuration from surfaces.

Figure 4. Laser desorption ionization mounted to interface with the MS inlet

We applied a Continuum Minilite ML II Nd:YAG laser (355 nm, 5 mJ/pulse) to operate as a laser ablation ionization source. The beam path employs a 75-mm lens and a single high power laser mirror to focus the ablation spot to 2.52 mm ahead of LCQ inlet. A sample stage is mounted horizontally in close proximity. The beam spot is illuminated in the figure 4 above. The laser fluence we are able to achieve amounts to 200.48 kW/mm^2 which does not produce ions in the ablation regime from solid metals. Preformed ions however, in the form of soluble salts, provide a more easily accessible desorption ionization regime.

API-MS Interface

A planar DMS cell adapted from a Vespel polyamide features two 15mm long and 4mm wide rectangular electrodes separated by 0.05 mm gap (figure 5). The electrodes are screwed in to maintain a constant gap distance within the cell and to allow V_{rf} and V_c voltage potentials supplies by the Sionex electronic hardware. The DMS cell is set with a face-sealed o-ring to sit flush against the interface and minimize losses to the MS. The design is anticipated to accommodate external pumping and sensor probes. The probes are meant to monitor the humidity, temperature, and pressure of the DMS carrier gas as it exits the DMS channel. Redundant features ahead of the DMS cell can then be used to validate gas conditions are maintained through the DMS.
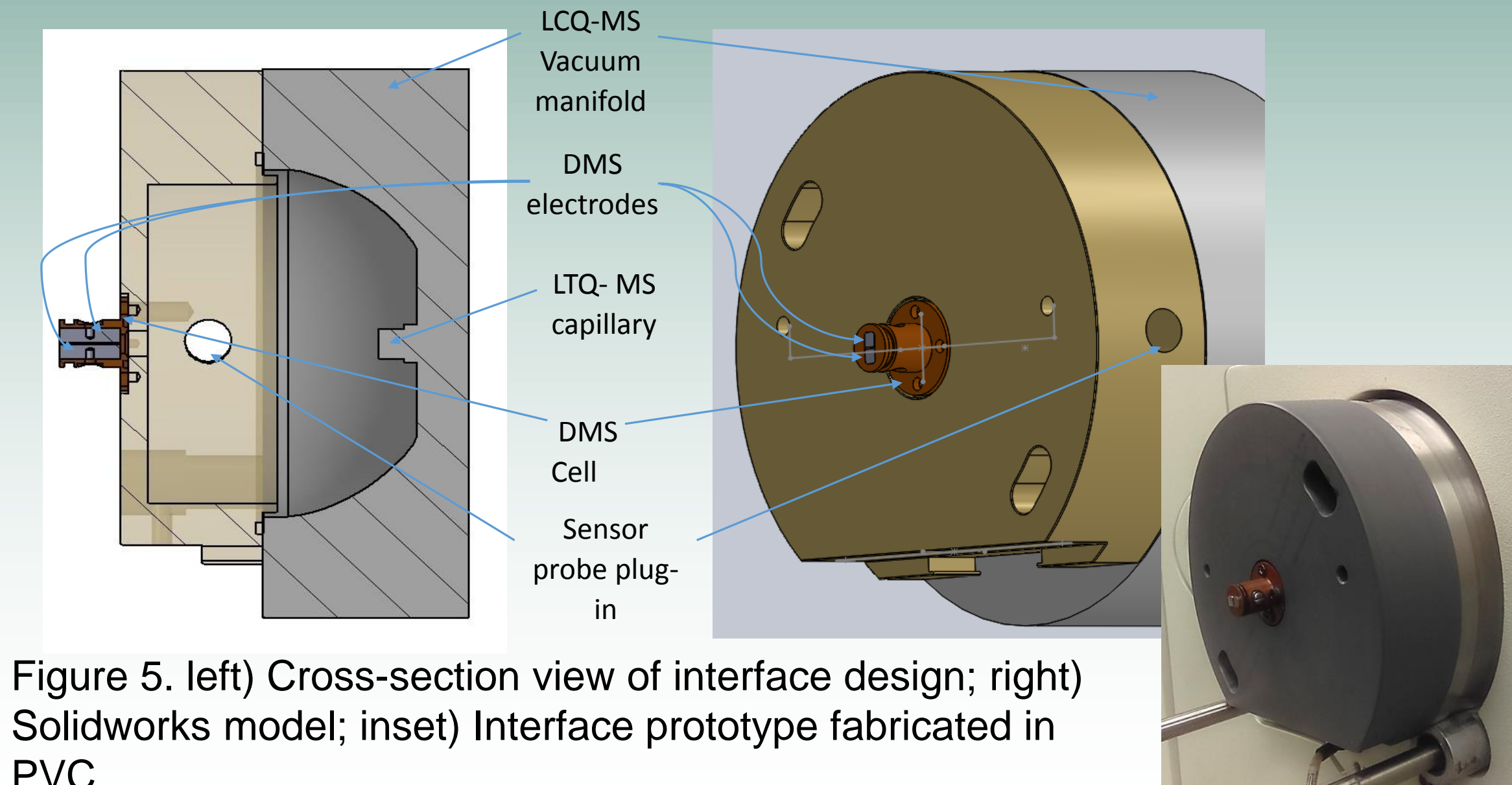

Figure 5. left) Cross-section view of interface design; right) Solidworks model; inset) Interface prototype fabricated in PVC.

Conclusions

We have begun iterating preliminary designs to systematically introduce metal cations into a home-built DMS-MS system. While access to a laser ablation regime for ion production did not appear achievable with the low powers of our current laser capabilities, a desorption ionization mechanism such as that leveraged in AP-MALDI may provide us optimal dry conditions for more robust ion introduction into DMS. To further systematically control DMS operational conditions, we also sought to independently constrain DMS flow by building, into the existing interface design, a port to provide external pumping. The interface design further allows us to adapt a DMS chamber, itself designed to simply and efficiency transfer ions.

Future Directions

We intend to ultimately design and fabricate a reaction chamber to rigorously monitor and control the ion-cluster formation. We will employ a calibrated vapor generator to control the DMS carrier gas humidity independently from the ionization source through this chamber. This design shall be facilitated by fluid dynamic modeling of gas transport supported by ion transport models through SIMION. Experimental data obtained from the V_{rf} and V_c transmission conditions shall be translated to their effective alpha parameters for comparison. Exploration of controlled ionization drying for nanoelectrospray conditions will help to determine ideal conditions impacting DMS separation from water clustering phenomena. We intend to correlate water-mitigated DMS metal ion behavior with chemical modeling to further complement ion mobility analyses. Additionally, assembly of simplified, non-proprietary COTS electronics are anticipated to achieve higher E/N values and thereby extend the understanding of cluster behavior from hydration energies.

Acknowledgements

References

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