

## 2018 WORKSHOP OF THE ASMS METAL ION COORDINATION INTEREST GROUP

### THE ROLES OF METALS IN ION CHEMISTRY AND STRUCTURE: IN HONOR OF THE LATE ROBERT C. DUNBAR

#### *Interest Group Coordinators:*

***Eric D. Dodds, University of Nebraska – Lincoln***

***Nicolas C. Polfer, University of Florida***

***Tuesday, June 5, 2018, 5:45 - 7:00 pm***

#### **OVERVIEW**

The Metal Ion Coordination Interest Group proposed to offer a broadly themed workshop in honor of Prof. Robert C. Dunbar (Case Western Reserve University), who sadly passed away in later 2017. Topics of interest were selected to incorporate new experimental and theoretical insights that are inspired by some of Rob's work in the area of metal ion coordination. As the agenda for the workshop began to take shape, a theme emerged for the program and discussion: "*The Black Box of Metal Ions and Counter Ions in Electrospray Ionization: Experimental and Computational Perspectives on the Charging Conditions in Droplets.*"

#### **PROGRAM**

- 1. *Nicholas C. Polfer (University of Florida):*** Nick provided some introductory remarks to kick off the workshop, taking the opportunity to highlight some of Rob's many contributions to the field of metal ion binding in mass spectrometry. To set the stage for the rest of the program, Nick also outlined some currently unanswered fundamental questions on the topic of metal ions in ESI.
- 2. *Styliani (Stella) Conostas (University of Western Ontario):*** Stella gave a presentation on "*Computational Evidence of Charging Mechanisms of Macromolecules in ESI droplets.*" The work described a range of theoretical treatments of the ESI process, including the possibility of unusual charged droplet deformations (e.g., star-like shapes) contributing to the ionization process; the extrusion of charged species from ESI droplets; and the effects of metal ions and counter ions on the charging of analytes. Cases considered included double-stranded DNA, noncovalent protein complexes, and polyethylene glycols.
- 3. *Evan R. Williams (University of California Berkeley):*** Evan led a discussion on "*Suppressing Salt Adduct Formation.*" In protein analysis by ESI, the presence of nonvolatile salts lowers signal-to-noise ratios by virtue of both ion suppression (salt cluster formation) and the presence of multiple adducted species which splits the total signal over many more peaks. Several strategies for circumventing these challenges were summarized and discussed, including the use of ion-ion chemistry, droplet-vapor chemistry, the use of solution additives, and the use of ESI emitters with very small (hundreds of nm) openings.
- 4. *Valerie Gabelica (University of Bordeaux / Inserm / CNRS):*** Valerie raised a question on the "*Supercharging of Nucleic Acids in the Presence of Metal Ions.*" She observed that a single-stranded DNA 21-mer in the presence of 1% sulfolane gave rise to higher negative charge states than in the absence of sulfolane; however, counterintuitively, these higher negative charge state ions exhibited a greater degree of nonspecific cation adduction. Ion mobility data suggests multiple conformations of the DNA may be involved, though the strand is known to be unstructured in solution.

#### **NOTES**

The program began at 5:45 pm, and concluded at 7:00 pm. The relatively small number of workshop panelists facilitated some extensive discussions over the topics covered. The estimated peak attendance was approximately 65, while the estimated total attendance was approximately 80.