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Foreword

Mass spectrometry has become a key tool for solving difficult problems in biochemistry and biology. Both electrospray ionization and matrix-assisted laser desorption/ionization have opened new vistas in research in which mass spectrometry can now play a role. In conjunction with the advances in ionization methods, there have been rapid advances made in instrumentation, detection and tandem mass spectrometry methods. For example, new instrumentation and methods in time-of-flight mass spectrometry have enabled accurate mass measurements of high *m*/*z* ions, such as those typically formed by MALDI. External ion sources and ion injection methods in Fourier-transform and ion trap mass spectrometry have enabled coupling of electrospray ionization to these instruments. This has enabled a host of novel ion structural methods via tandem mass spectrometry, including gas-phase H/D exchange, electron capture dissociation, ion–ion reactions, chiral ion–molecule reactions, etc. These, and a wide array of other methods, have dramatically changed the field of mass spectrometry and ion chemistry.

While it is widely recognized that mass spectrometry is the method of choice for determining accurate molecular weights of biopolymers, there are competing methods for obtaining structural information that offer advantages over mass spectrometry. For example, the vast majority of DNA sequencing is performed by using a combination of Sanger chemistry, gel separations, and fluorescent detection. NMR and X-ray crystallography offer exquisite accuracy for obtaining the tertiary structure of biopolymers and their complexes. For some structural problems, however, the speed, specificity, and sensitivity of tandem mass spectrometry provides key advantages. For example, tandem mass spectrometry is often the method of choice to locate binding sites and sites of posttranslational modifications in proteins, examine dynamics of rapid protein folding/unfolding via H/D exchange in solution, and identify proteins either by means of direct dissociation or by sequencing the peptides formed by tryptic digests.

With the tremendous advances being made in the applications of mass spectrometry to biochemical analysis, it is important that a fundamental understanding of the gas-phase chemistry and structure of biopolymers be pursued. By understanding the chemistry that occurs in the gas phase, our ability to extract structural information from biopolymers is enhanced. Spectroscopy, ion mobility, gas-phase H/D exchange, and slow dissociation methods, such as blackbody infrared radiative dissociation, have offered a glimpse into how some aspects of solution-phase structure can be preserved in the gas phase. Gas-phase studies also offer the opportunity to examine the structure of biopolymers in the absence of water. In doing so, mass spectrometry provides the ideal method to fully understand the role of water on structure.

This issue contains a sampling of some of the excellent work that is being done in understanding the structure and energetics of gas-phase biopolymers. No special issue in this area can be complete, and

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there was no attempt to be comprehensive in this sampling. Rather, the 22 articles in this issue represent a snapshot of the exciting work that is being done in this field.

We thank each of the authors for contributing to this special issue and for their timely submission and revisions. Similarly, we thank all of the anonymous reviewers who make publication of peer review research possible. Finally, we thank Prof. Michael T. Bowers who originally suggested this special issue and who has been an enthusiastic supporter and active participant in extending gas-phase studies to large biopolymers. We hope that you enjoy this issue.

Evan R. Williams,
Department of Chemistry, University of California
Berkeley, CA 94720-1460, USA
E-mail: williams@cchem.berkeley.edu

Vicki H. Wysocki
Department of Chemistry, University of Arizona
Tucson, AZ 85721-0041, USA
E-mail: vwysocki@u.arizona.edu