Principles of Mass Spectrometry Applied to Biomolecules

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John Wiley & Sons, Inc.
Hoboken, NJ 07030
2006, Hardcover, $150.00, 687 pp.
ISBN: 978-0-471-72184-0

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Principles of Mass Spectrometry Applied to Biomolecules is an interesting representation of an impressive variety of different aspects of biological mass spectrometry. The editors point out that, although the fundamental studies of ionic properties were incredibly successful when applied to small organic species several decades ago, the explosive growth of biological mass spectrometry poses a new set of challenges. Further improvements of biomolecular analysis using modern mass spectrometry require better understanding of fundamental aspects of biomolecular ions in a solvent-free environment. Large size, conformational diversity, and the ability of biopolymers to accommodate multiple charges are the three major factors that contribute to the increasingly complicated relationship between the biomolecular primary structure and the properties of corresponding ionic species in the gas phase. A unique aspect of the book is that it attempts to bring together physical chemists involved in the fundamental studies of biomolecular ions in the gas phase and mass spectrometry practitioners focused on increasing the scope of application of this technique to various problems in life sciences. It is no secret that these two groups do not always interact very actively and any attempt to initiate such a conversation is likely to benefit both.

The book is divided into three parts; grouping sections related to structural aspects of biomolecules in the gas phase (Chapter I), physical phenomena related to dissociation and reactivity in general (Chapter II), and gas-phase thermodynamics (Chapter III). Rigorous studies of macromolecular ions (both experimental and theoretical) are incredibly difficult and it is not surprising that most of the contributions in Chapter I deal with very small model systems, such as single amino acids. The only exception is a contribution by Sobott and Robinson, who consider various factors related to the fate of large macromolecular assemblies in the gas phase. Breuker presents a general overview of techniques used to probe higher-order structure of polypeptide ions in the absence of solvent. Other contributions focus on spectroscopic methods applied to structural studies of small bioions (Gerhards) and inorganic clusters (Yang et al.), use of hydrogen exchange in the gas-phase (Green and Lebrilla), as well as theoretical methods to simulate amino acid photoionization (Shemesh and Gerber). The chapter concludes with an overview of both experimental and theoretical methods to study energy redistribution in ions of organic molecules and small peptides (Lifshitz).

Coverage of dissociation of biomolecular ions in Chapter II includes a very detailed overview of peptide ion fragmentation phenomena by Wysocki and coworkers, as well as more focused discussion of electron capture dissociation (Zubarev) and photodissociation (Dunbar). Hopkinson and Siu discuss fragmentation behavior of peptide radical cations and Rahaman et al. provide an overview of computational methods to simulate energy transfer within and dissociation of protonated amino acids and inorganic cations upon collisional activation. Other aspects of peptide and protein ion reactivity are reflected in contributions of McLuckey (ion–ion reactions) and Cooks and coworkers (ion soft landing).

The third chapter contains a very detailed overview of various aspects of thermochemistry of small biomolecular ions by Wesdemiotis and Wang and a contribution by Laskin focused on energetic and entropic determinants of peptide ion fragmentation in the gas phase.

When such an impressive volume is put together, some things inevitably are missed. The editors did a wonderful job in minimizing such gaps. Perhaps the book could have benefited from the inclusion of sections considering other types of biomolecules in addition to peptides and proteins. Mass spectrometry has already become a valuable practical tool in oligonucleotide and polysaccharide research, and several studies of intrinsic gas-phase properties of these biopolymers were recently reported. Initiating a cross talk between physical chemists involved in fundamental studies and biologists interested in expanding the capabilities of mass spectrometry in glycobiology and oligonucleotide analysis is likely to catalyze new exciting developments in these fields.

Overall, this is a very impressive volume, which I recommend to anyone interested in fundamental principles governing peptide and protein ion behavior in the gas phase.

Published online February 14, 2007

1044-0305/07/$32.00
doi:10.1016/j.jasms.2007.01.007
(J Am Soc Mass Spectrom 2007, 18, 802)