Preface

Spectroscopy of isolated biomolecular ions *in vacuo* has within the last decade or so become a highly active research field, both for experimentalists and theorists, made possible by the development of advanced instrumental apparatus and the steady increase in more powerful computers. The field is highly interdisciplinary including researchers in chemistry, physics, and molecular biology. Absorption spectra of isolated ions shed light on the intrinsic electronic structures without perturbations from say water molecules, counter ions, nearby charges, or polar amino acids. A comparison with spectra of the chromophores in their natural environment then allows one to identify possible perturbations. Spectra at the same time provide important benchmarks for quantum chemical calculations of electronically excited states, which is still a non-trivial task. Not only absorption spectra but also fluorescence spectra are excellent indicators of environmental effects. In this volume, we focus on spectroscopy of protein chromophores, amino acids and peptides, to whole proteins and DNA nucleotides and oligonucleotides. Dissociation channels and timescales for deexcitation and dissociation are also discussed in detail, as they shed important light on energy-flow processes within the isolated biomolecular ion; indeed, small molecular ions with few degrees of freedom are destined to break apart after photoexcitation due to the absence of a heat bath (energy sink). As all systems included here are ionic, mass spectrometry in combination with lasers are used for the experiments. Experimental techniques to measure spectra and theoretical methods commonly employed are described with a discussion on limitations and advantages.

Our book comprises 11 chapters each written by one or more experts in the topic. The book is organised as follows: At the beginning of the book, even before the General Introduction, there are explanatory pages (Concepts) for non-experts in the field where we briefly describe electric- and magnetic-field sectors used as ion deflectors, photophysical processes illustrated by Jablonski diagrams, molecular orbital theory, solvatochromic shifts of electronic transitions, peptide and nucleic acids structures, and nomenclature regarding peptide fragmentation. Our hope is that with these sections, the book shows potential to be used for graduate teaching courses in photobiology and not just for researchers within the field. The second chapter is a brief introduction by one of us (Brøndsted Nielsen) discussing

biochromophore ions and the role of microenvironments such as water or nearby charge sites. The chapter ends by touching upon possible future directions for the field. In the next chapter, Wyer introduces the experimental techniques used for performing gas-phase spectroscopy of ions with emphasis on ion storage rings and other home-built ion beam set-ups as these are less well described in the literature. It is certainly true that no experiment is perfect, and Wyer discusses the advantages and disadvantages with different set-ups, differences between positive and negative ions and importantly what to be cautious about when interpreting experimental results. In the next chapter by Rubio and Wanko, theoretical methods that are commonly employed to describe these rather big systems are presented. Also here the methods are carefully evaluated and their performances relative to each other are discussed. The subsequent chapters deal with actual biochromophores and their photophysics. The chapter by Andersen and Bochenkova gives an overview of the GFP chromophore anion and its absorption spectrum; this spectrum from 2001 was the first to be obtained for an isolated biochromophore ion. The authors discuss the competition between electron photodetachment and internal conversion, which is an issue that needs to be considered for anions whose detachment energies are within the absorption band. The next chapter by Brøndsted Nielsen deals with the detection of light emitted from photoexcited chromophore ions (dyes), which is even harder experimentally than obtaining an absorption spectrum. Still fluorescence spectroscopy has proven to be a very strong tool for monitoring structures of isolated biomolecular ions. Wyer and Brøndsted Nielsen summarise in the following chapter the increasing amount of data on porphyrin and heme ions and their complexes with amino acids and NO and compare results with protein spectra. Also two-laser experiments are discussed allowing one to record spectra of long-lived photoexcited ions. Spectra of whole proteins are presented in the next chapter by Antoine and Dugourd, where either heme or aromatic amino acid residues are the absorbing species. The authors demonstrate the importance of the charge state in obtaining action spectra, and from two-laser experiments they nicely succeed in performing spectroscopy on radical species. Dedonder, Féraud, and Jouvet provide a comprehensive review of the field of spectroscopy of protonated amino acids and small peptide ions, both at room temperature and at low temperature, with emphasis on the fast dissociation channels that are operative when the ions are electronically excited and that compete with internal conversion to the electronic ground state; their relative importance is measured from photodissociation of the ions in an electric field. The number of fragments formed in a dissociation process is found from coincidence experiments considering momentum conservation. Timescales for the deexcitation processes are established from femtosecond pump-probe laser experiments. Their work nicely demonstrates how experimental results and theoretical ones go hand in hand in obtaining the deepest level of understanding. DNA and RNA nucleotides and oligonucleotides are the focus of the chapter by Weber, Marcum, and Brøndsted Nielsen who in detail discuss UV-induced fragmentation channels, timescales for dissociation after photoexcitation and whether dissociation is statistical or nonstatistical, and finally electronic spectra (both absorption and photoelectron spectra). In this chapter the complex role of multiple light absorbing

species is also considered. In all of these works either visible or UV light was used for the experiments. In the final chapter by Schlathölter and Hoekstra, recent work in extending the wavelength region to the vacuum ultraviolet is presented, and the importance of this region is clearly emphasised by work on peptide ions.

Let us end by saying that the chosen topics for this volume present a selection of important scientific contributions that *we* believe have been made to this rapidly increasing field. They are of course biased by our own interests, and other important work could have been covered, *e.g.* the electronic properties of simpler molecular ions isolated *in vacuo* that were earlier explored. However, we hope that the reader has got an impression after reading all the chapters of the rich possibilities that exist to form and study complicated and fragile ions *in vacuo*, and that, most importantly, new fundamental science is learned from such work. We would like to take the opportunity to thank all the authors who have contributed to this volume and in our opinion have made this volume a most timely one and one of very high quality.

Aarhus, June 25, 2013 Steen Brøndsted Nielsen and Jean Ann Wyer

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