

PREFACE

Photoionization and photodetachment processes are the simplest electron transfer reactions induced by photoabsorption. Thus, the understanding of these processes is of fundamental importance to physics, chemistry and biology. Although the physics and chemical applications of photoionization and photodetachment have much in common, these areas have been arbitrarily viewed as two different research fields in the past. Considering the similarity in experimental techniques used for the study of photoionization and photodetachment processes, the lack of communication between researchers in these research fields is surprising. Due to the low electron affinities of atomic and molecular species, photodetachment studies can be made using commercially available high-resolution visible and ultraviolet (UV) lasers. The high ionization energies (IEs) for atomic and molecular species require the use of vacuum ultraviolet (VUV) light sources for single-photon ionization studies. The recent development of VUV lasers and third generation synchrotron sources, together with the introduction of the pulsed field ionization photoelectron (PFI-PE) and ion detection schemes, has significantly broadened the scope of VUV photoionization and photoelectron studies. With these technical advances, it is now possible to measure rovibronically state-resolved transitions in photoionization of diatomic and simple polyatomic molecules. Thus, the resolution gap between photoionization and photodetachment studies has essentially been eliminated. The reverse processes of photoionization and photodetachment are electron-ion recombination and electron attachment, respectively. Significant experimental progress has also been made in the studies of these processes. This two-volume review represents the first attempt to present the topics of photoionization, photodetachment, electron-ion recombination, and electron attachment in a unified manner, covering some of the most important experimental and theoretical developments in recent years.

Volume 10A consists of twelve chapters. In Chapter 1, Parker gives a detailed account of the velocity-imaging method, a new variant of the ion imaging technique, for the investigation of photodissociation and dissociative photoionization processes. It is shown that an immersion lens can be used to map all ions with the same velocity to the same point on a two-dimensional detector, irrespective of their positions of origin. This velocity-imaging scheme is expected to make its way into experimental studies employing linear time-of-flight ion detection schemes, especially in experiments involving the use of a position sensitive detector. Gordon and Zhu describe in Chapter 2 the first experimental demonstration on the control of dissociative photoionization channels by employing the coherent phase control scheme originally proposed by Brumer and Shapiro. The focus of Chapters 3 and 4 is on the development and application of femtosecond laser time-resolved photoelectron and photoionization techniques for studies of radiationless relaxation processes, dissociation dynamics, and photochemical reactions in molecules and molecular clusters. The femtosecond laser pump-probe approach together with photoelectron detection schemes promises to add a new dimension for molecular dynamics studies. High-resolution spectroscopic experiments demand detailed theoretical interpretations. Rosmus and Chambaud review in Chapter 5 some highly accurate *ab initio* theoretical calculations, focusing on the interpretation of spectroscopic data for selected molecular ion systems in terms of Renner–Teller interactions and anharmonic resonances. The role of degenerate electronic states in the stability, protonation, charge transfer, and photodissociation of small molecular ions are also discussed from the theoretical perspective. In Chapter 6 Kimura summarizes selected PFI-PE studies of aromatic-Ar van der Waals (vdW) complexes using two-color laser excitation schemes. These high-resolution photoelectron measurements have yielded accurate vibrational and structural information for these complexes. The detection of mass-analyzed threshold ions (MATI) formed in PFI is first introduced by Johnson. In addition to reviewing the MATI scheme, Johnson also presents in Chapter 7 an ion spectroscopic technique, photoinduced Rydberg ionization (PIRI) spectroscopy, involving the detection of ions produced by photoexcitation of high- n Rydberg species. The availability of modern synchrotron radiation sources has been a key factor for the recent progress in VUV photoionization and photoelectron studies. Chapter 8 by Morioka reviews high-resolution synchrotron based threshold photoelectron (TPE)

and TPE-photoion coincidence (TPEPICO) measurements on diatomics and rare-gas dimers using the penetrating field scheme. Ng provides in Chapter 9 a detailed account of experiments performed using the newly developed synchrotron based PFI-PE detection scheme at the Chemical Dynamics Beamline of the Advanced Light Source (ALS). Selected UV/VUV laser PFI-PE experiments on simple polyatomic molecules are also discussed with the emphasis on developing a semi-empirical simulation scheme for accurate IE determinations. Chapter 10 by Weitzel is devoted to unimolecular kinetics and dynamics studies using synchrotron based TPEPICO methods and two-color laser resonant enhanced multiphoton ionization schemes. The use of a reflection time-of-flight mass spectrometer in TPEPICO studies has made possible the measurement of dissociation rates in the range of 10^{-3} – 10^{-7} s $^{-1}$ for energy-selected molecular ions. Photoionization and photoabsorption studies of liquids represent an unexplored research area. The review of Chapter 11 by Ogawa concerns the development of two-photon laser ionization schemes as sensitive molecular detection methods based on conductivity measurements in solution and on surfaces in ambient air. Faubel pioneers the technique for the formation of liquid jets in high vacuum, allowing photoelectron studies of the liquid surfaces in collision free environments. He presents in Chapter 12 the experimental consideration for the formation of liquid jets in vacuum and the essence of selected photoelectron experiments involving the study of solutions in the form of liquid jets.

Volume 10B comprises of Chapters 13–22. The central theme of Chapter 13 by Larsson is on the study of dissociative electron–ion recombination processes using ion synchrotrons. The cross-section measurements for electron–ion recombination reactions are among the most difficult experiments. The recent ion synchrotron experiments can be considered a technical breakthrough and promise to provide fundamental insight into these complicated processes. Continetti reviews in Chapter 14 the recent development in combining the multi-coincidence and dissociative photodetachment methods for studying the energetics and dissociation dynamics of transient neutral species. This multi-coincidence scheme requires the use of a time and position sensitive detector and is directly applicable for studies of dissociative photoionization processes. Similar to PFI-PE spectroscopy on cations, anion-zero kinetic energy (ZEKE) photoelectron spectroscopy is a special development of photoelectron spectroscopy on anions. The resolution achieved in anion-ZEKE studies are usually more than an order

of magnitude better than conventional anion-photoelectron spectroscopy. In Chapter 15, Boesl *et al.* reviews the results of recent anion-ZEKE studies. By using laser ablation for the preparation of non-volatile metal oxides, Wang has performed a series of anion-photoelectron studies of transition metal oxides, yielding valuable energetics and structural information for these oxides. The results of these studies are summarized in Chapter 16. In Chapter 17 Simons presents the theory for underlying electron detachment mechanisms in molecular anions, including detachment induced by photoabsorption, collisions, and intramolecular energy transfers. In accordance with the detachment mechanisms, various kinds of stability for anions are classified. The focus of Chapter 18 by Pratt is on the decay processes of molecular Rydberg states at energies higher than the first IE of the molecule. Since such Rydberg resonances may decay by autoionization and/or neutral dissociation, the study of such decay processes is relevant to dissociative recombination. Illenberger reviews in Chapter 19 molecular decay processes induced by electron capture at electron kinetic energies below the IE of the molecule. This chapter gives special emphasis on electron attachment reactions in binary vdW complexes and on dissociation processes of molecules adsorbed on metallic substrates and condensed molecules. The study of electron correlations and many-body interactions from first principle calculations is a main concern of theoretical research in atomic and molecular physics. Lin and Morishita present in Chapter 20 first principle calculations on doubly and triply excited states of atoms using hyperspherical coordinates. These theoretical studies reveal interesting symmetry properties for the joint motions of two and three electrons in doubly and triply excited atomic states, respectively. Chapter 21 by Berrah reports some recent state-of-the-art photoionization and photoelectron experiments conducted at the high-resolution atomic and molecular beamline of the ALS, covering the photon energy range of 25–350 eV. These experiments have yielded new observations and insights into many-body interactions in excited atomic and molecular states. The interpretation of these experimental results has also presented new challenges to the development of atomic and molecular theories. In this Chapter 22, Southworth *et al.* discuss the basic physics of X-ray interactions with atoms and molecules, together with illuminating examples of elastic and inelastic X-ray scattering experiments using X-ray beamlines at the National Synchrotron Light Source and the Advanced Photon Source.

In addition to presenting the recent technical and scientific progress, individual chapters also contain an expert assessment of the future research directions. It is my hope that this review will become a useful reference for graduate students and new researchers interested in the subject of photoionization and photodetachment. Finally, I would like to thank all contributors of Vols. 10A and 10B for their energy and enthusiasm devoted to this project. The opportunity for me to read and appreciate their state-of-the-art scientific writings was my best Christmas present.

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