DISSOCIATIVE RECOMBINATION OF MOLECULAR IONS

Dissociative recombination (DR) of molecular ions with electrons is a complex, poorly understood molecular process. Its critical role as a neutralizing agent in the Earth's upper atmosphere is now well established and its occurrence in many natural and laboratory produced plasmas has been a strong motivation for studying the event. For the first time, theoretical concepts, experimental methodology, and applications are united in one book, revealing the governing principles behind the gas-phase reaction. The book takes the reader through the intellectual challenges posed, describing in detail dissociation mechanisms, dynamics, diatomic and polyatomic ions, and related processes, including dissociative excitation, ionpair formation and photodissociation. With the final chapter dedicated to applications in astrophysics, atmospheric science, plasma physics, and fusion research, this is a focused, definitive guide to a fundamental molecular process. The book will appeal to academics within physics, physical chemistry, and related sciences.

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We would like to dedicate this book to Sheldon Datz, who was responsible for introducing us to this interesting area of physics.

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Preface

This research monograph provides a single-volume description of the dissociative recombination of molecular ions with electrons. Since this is one of the most complex gas-phase processes, its study is a challenge to theorists and experimentalists alike. The theory, experiment, and applications of dissociative recombination are scattered in the scientific literature as original research articles, conference proceedings, and review articles. This book brings this information together in a single work for the first time.

The book is intended for researchers and Ph.D. students in the fields of atomic and molecular physics, chemical physics and physical chemistry, molecular astrophysics, atmospheric physics, and other areas of science where electrons and molecular ions are important.

This book was written during a period when each of us had several other commitments which slowed down the writing. One of us (AEO) was department chair at UC Davis essentially during the entire writing process, and ML chaired committees for the Swedish Space Board and the Swedish Research Council.

We are grateful for the hospitality of the Institute for Atomic and Molecular Physics (ITAMP) at the Harvard-Smithsonian Center for Astrophysics and Harvard University Physics Department (Kate Kirby, Hussein Sadeghpour), the Cluster Research Laboratory, Toyota Technological Institute, Tokyo (Tamotsu Kondow), and the University of Chicago (Takeshi Oka), all of which provided excellent working conditions for us when we needed to get away from our home institutions to focus on writing.

Several people have assisted us in reading part of the book and making valuable suggestions: Alex Dalgarno, Shirzad Kalhori, Holger Kreckel, Åsa Larson, Valery Ngassam, Takeshi Oka, Jeanna Royal, Albert Viggiano and Vitali Zhaunerchyk. We offer them our sincerest thanks for their help.

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Dissociative recombination (DR) of the dimer ion (NO)2+ has been studied at the heavy-ion storage ring CRYRING at the Manne Siegbahn Laboratory, Stockholm. The experiments were aimed at determining details on the strongly enhanced thermal rate coefficient for the dimer, interpreting the dissociation dynamics of the dimer ion, and studying the degree of similarity to the behavior in the monomer.Â The rate of dissociative electron capture by heavy molecular ions is developed in the semiclassical formalism. The quantum treatment of the rate coefficient is also outlined. Dissociative Recombination of diatomic molecular ions with electrons is of great interest because of the importance of the process in many regions of Earth's ionosphere, in laboratory plasma, gaseous lasers and more generally in chemical processes. The Dissociative Recombination (DR) of helium molecular ions is of particular interest because of "the terrestrial helium problem" [1] which refers to the apparent imbalance between the atmospheric sources and sinks of helium. The main source of atmospheric helium is the radioactive decay in the natural radioactive series of uranium a The molecular data necessary to model the dissociative recombination and rotational excitation are the potential energy curve (PEC) of the ground state of the ion, the PECs of the neutral valence dissociative states interacting with the ionization continua, those of the Rydberg states associated to these continua below the threshold (leading to smooth R-dependent quantum defects) and all the relevant Rydberg-valence.Â [13], given in Figures 3 and 4 of the same reference and are shown on the right side of Figure 1. Using this set of molecular data (PECs, electronic couplings and quantum defects), we performed a series of full rotational MQDT calculations of the cross sections for dissociative recombination for vibrationally relaxed CH. + molecular ions on their first 11 rotational levels. Dissociative recombination is a process where a positive molecular ion recombines with an electron, and as a result, the neutral molecule dissociates. This reaction is important for extraterrestrial and atmospheric chemistry. On Earth, dissociative recombination rarely occurs naturally, as free electrons react with any molecule (even neutral molecules) they encounter. Even in the best laboratory conditions, dissociative recombination is hard to observe, but is an important reaction in systems that