

Kinetics of Ion-Molecule Reactions

NATO ADVANCED STUDY INSTITUTES SERIES

A series of edited volumes comprising multifaceted studies of contemporary scientific issues by some of the best scientific minds in the world, assembled in cooperation with NATO Scientific Affairs Division.

Series B: Physics

RECENT VOLUMES IN THIS SERIES

- Volume 32* – Electron and Ion Spectroscopy of Solids
edited by L. Fiermans, J. Vennik, and W. Dekeyser
- Volume 33* – Microscopic Structure and Dynamics of Liquids
edited by J. Dupuy and A. J. Dianoux
- Volume 34* – Path Integrals and Their Applications in Quantum,
Statistical, and Solid State Physics
edited by George J. Papadopoulos and J. T. Devreese
- Volume 35* – Correlation Functions and Quasiparticle Interactions
in Condensed Matter
edited by J. Woods Halley
- Volume 36* – Strongly Coupled Plasmas
edited by Gabor Kalman
- Volume 37* – Coherence in Spectroscopy and Modern Physics
edited by F. T. Arecchi, R. Bonifacio, and M. O. Scully
- Volume 38* – Theoretical Methods in Medium-Energy and Heavy-Ion Physics
edited by K. W. McVoy and W. A. Friedman
- Volume 39* – Hadron Structure and Lepton–Hadron Interactions – *Cargèse 1977*
edited by Maurice Lévy, Jean-Louis Basdevant, David Speiser,
Jacques Weyers, Raymond Gastmans, and Jean Zinn-Justin
- Volume 40* – Kinetics of Ion–Molecule Reactions
edited by Pierre Ausloos
- Volume 41* – Fiber and Integrated Optics
edited by D.B. Ostrowsky



The series is published by an international board of publishers in conjunction with NATO Scientific Affairs Division

A Life Sciences	Plenum Publishing Corporation
B Physics	New York and London
C Mathematical and Physical Sciences	D. Reidel Publishing Company Dordrecht and Boston
D Behavioral and Social Sciences	Sijthoff International Publishing Company Leiden
E Applied Sciences	Noordhoff International Publishing Leiden

Kinetics of Ion-Molecule Reactions

Edited by

Pierre Ausloos

United States Department of Commerce

National Bureau of Standards

Washington, D.C.

PLENUM PRESS • NEW YORK AND LONDON

Published in cooperation with NATO Scientific Affairs Division

Library of Congress Cataloging in Publication Data

Nato Advanced Study Institute on Kinetics of Ion-Molecule Reactions, La Baule, 1978.

Kinetics of ion-molecule reactions.

(Nato advanced study institutes series: Series B, physics; v. 40)

Includes bibliographical references and index.

1. Chemical reaction, Conditions and laws of—Congresses. 2. Ions—Congresses. 3. Molecules—Congresses. I. Ausloos, Pierre J. II. Title. III. Series.

QD501.N37 1978 541'.39 79-367

ISBN-13: 978-1-4613-2933-6 e-ISBN-13: 978-1-4613-2931-2

DOI: 10.1007/978-1-4613-2931-2

Proceedings of the NATO Advanced Study Institute on Kinetics of Ion-Molecule Reactions held at La Baule, France, September 4–15, 1978

© 1979 Plenum Press, New York

Softcover reprint of the hardcover 1st edition 1979

A Division of Plenum Publishing Corporation
227 West 17th Street, New York, N.Y. 10011

All rights reserved

No part of this book may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording, or otherwise, without written permission from the Publisher

Preface

The investigation of the elementary reactions of reactive intermediate species began about half a century ago with the advent of free radical kinetics as an active area of chemical research. In spite of the relatively greater ease of detection of a species carrying an electrical charge, and the fact that organic chemists had for decades postulated mechanisms involving ionic intermediates, the systematic study of the elementary reactions of ions was delayed for more than twenty years after the first beginnings of free radical kinetics. Even at this writing, in 1978, the word "kinetics" is considered by many chemists to be synonymous with "kinetics of neutral species".

Yet in spite of the relatively late start and separation from the mainstream of kinetics, the field of ion physics and chemistry is flourishing, and growing at an ever faster pace. Instrumentalists devise ever more sophisticated apparatuses with capabilities of delving into nearly every aspect of the interactions between ions and molecules. Even satellites orbiting the earth are now being used effectively to determine rate coefficients of ionospheric ion-neutral reactions, some of which can not as yet be measured in the laboratory.

This book contains discussions of some of these new experimental approaches and the resulting knowledge which has been acquired since the earlier 1974 NATO Advanced Study Institute on Interactions between Ions and Molecules, which was held in Biarritz, France. Besides the more fundamental aspects of ion kinetics and the characterization of ions with regard to structure and energy, ionic processes occurring in interstellar space, the earth's atmosphere, lasers, and combustion, are discussed here. In addition, readers will find chapters describing nucleation phenomena and the relationships between ionic processes occurring in the gas and liquid phases.

I would like to express my appreciation to everyone who contributed to the success of the NATO Advanced Study Institute on Kinetics of Ion-Molecule Reactions held at La Baule, France, in

September, 1978. This includes not only all of the lecturers, those who contributed to the discussion panels, and those who chaired the sessions, but, just as important, all of those in attendance whose interest and enthusiasm contributed to the stimulating atmosphere of the Institute. I would also like to give recognition to the efforts of the members of the Organizing Committee Rose Marx, Sharon Lias, Keith Jennings, Paul Kebarle, Eldon Ferguson, and especially Tom Govers, who was largely responsible for the smooth functioning of the physical details of the meeting. On behalf of all participants, I would like to thank the Scientific Affairs Division of the North Atlantic Treaty Organization without whose financial assistance the occurrence of such a constructive summer school would not have been possible. I personally would like particularly to acknowledge the moral support supplied by the secretary of the Scientific Affairs Division, Dr. Tilo Kester. We also thank the National Science Foundation of the U.S.A. for travel grants.

P. Ausloos
Washington, DC
November, 1978

Contents

Potential Energy Surfaces for Ion-Molecule Reactions Panel Discussion Led by Joyce J. Kaufman	1
Ion-Dipole Collisions: Recent Theoretical Advances Walter J. Chesnavich, Timothy Su, and Michael T. Bowers	31
Ion-Molecule Collisions: Theory and Experiment Panel Discussion Led by Douglas P. Ridge	55
Ion-Molecule Collision Complexes Panel Discussion Led by Cornelius E. Klots	69
Molecular Beam Studies of Ion-Molecule Reactions W. Ronald Gentry	81
Charge Transfers at Thermal Energies: Energy Disposal and Reaction Mechanisms R. Marx	103
Energy Dependences of Ion-Neutral Reactions Studied in Drift Tubes Daniel Lee Albritton	119
Internal Energy Partitioning Panel Discussion Led by J. J. Leventhal	143
Factors Influencing Thermal Ion-Molecule Rate Constants John I. Brauman	153
Mechanistic Aspects of Ion-Molecule Reactions N. M. M. Nibbering	165

Intramolecular Selectivity, Stereochemical and Steric Aspects of Ion-Molecule Reactions Fulvio Cacace	199
Thermochemistry of Polyatomic Cations Sharon G. Lias	223
Equilibrium Studies of Negative Ion-Molecule Reactions Robert T. McIver, Jr.	255
Proton Transfer Reactions in the Gas and Solution Phase Robert W. Taft	271
Studies of Ion Clusters: Relationship to Understanding Nucleation and Solvation Phenomena A. W. Castleman, Jr.	295
Chemical Ionization in Flames D. K. Bohme	323
Ion-Molecule Reactions in Low Temperature Plasmas: Formation of Interstellar Species David Smith and Nigel G. Adams	345
Ion-Molecule Reactions in the Atmosphere Eldon E. Ferguson	377
Ion-Molecule Processes in Lasers James B. Laudenslager	405
Decay Processes of the Lowest Excited Electronic States of Polyatomic Radical Cations J. P. Maier	437
Ion Photodissociation Robert Dunbar	463
New Instrumentation for the Investigation of Ion-Molecule Reactions Panel Discussion Led by John R. Eyler (Prepared by Ben S. Freiser)	487
Index	499