This is the first book to describe the general features of ZEKE (ZEro Kinetic Energy) spectroscopy, a new high-resolution spectroscopy of molecular ions, neutral short-lived intermediates, and other species.

The author's approach is to use a minimum of equations and large numbers of figures to help the reader towards a basic understanding of the many unique concepts of this new form of spectroscopy and the new spectroscopic information that it provides. Since 1984 ZEKE spectroscopy has matured into a very-high-resolution spectroscopy for the study of cations, anions and, indirectly through these species, of neutral species, including very-short-lived intermediates in chemical reactions. It has even yielded the first direct spectroscopic data on elusive transition states of chemical reactions. It also provides measurement to a very high degree of accuracy and at a resolution three orders of magnitude better than those of other major techniques such as photoelectron spectroscopy. As such, it is able to generate useful new spectroscopic results using a reasonably straightforward experimental set-up.

For positive ions the technique derives its power from the newly discovered existence of certain very-long-lived neutral states of some 50–100 μs duration in a narrow band, some 8 cm^{-1} below each ionic state. These are hidden beneath the strong signal from ions that is always present in normal photo-ionization experiments. Stripping out the signal from these ions produces the ZEKE states, which may be sharpened into a spectroscopic signature of all ion states possible in the system. Such states exist even at much higher energies beyond ionization. For negative ions, this technique looks at the threshold directly since the electron is only weakly bound to the molecular system.

This book will be of interest to anyone interested in the spectroscopy of ions or of neutral species, particularly short-lived neutral species, formed from these ions. It should also be of interest to reaction kineticists interested in the study of reactions involving such highly state-selected species.

ZEKE SPECTROSCOPY

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Foreword

This book is meant as a primer to the field of ZEKE spectroscopy. Specifically, it attempts to transmit the flavour of the method together with some representative examples of the many applications of this new spectroscopy which are already in existence, by making extensive use of figures and pictures. It is meant to be pleasant reading as an overview of the whys and wherefores of this new spectroscopy – the approach is in line with the historical development, to show the essence of the new method as represented by its evolution, and to present representative examples of the already substantial body of knowledge accumulated in this field leading to a new spectroscopy. For a more formal and rigorous development, the reader is referred to the original literature or to one of the many review articles which now exist on **Z**ero **K**inetic **E**nergy (ZEKE) spectroscopy[1–3] as well as those which are presented on the current list of the World Wide Web (see the end of the book).

The new method was made possible in part by the discovery of ZEKE states; discussion of their origin involves a fascinating sojourn into some new aspects and discoveries of the properties of high-angular-momentum Rydberg molecules, which were not well known before. Only a phenomenological sketch of this physics is given, since this is a different topic in its own right. The usefulness and the applications of this new spectroscopy are legion. It is a new spectroscopy that makes unique use of photoelectrons at threshold. It expands the horizons of our understanding to new structures of import to modern chemistry.

For these lectures I will draw primarily on the work with my group here in Munich. These associates have formed over many years a closely coupled team generating many ideas and experiments that culminated in the groundwork for ZEKE spectroscopy. This cooperative effort has been principally with the group of Dr Müller-Dethlefs, but in addition the groups of

Dr Selzle, Professor Neusser, Dr Boesl, Dr Weinkauf, Dr Held and Dr Baranov have contributed in highly significant but differing ways to the joint effort here in Munich. All of us are joined in the closely intertwined effort of developing this new technique and hence I will refer to this effort in the text naturally as our work. All this work equally well and implicitly reflects many hours of discussions on theory with Professor R. D. Levine in Jerusalem and his associates.

This work, of course, historically was preceded by related work on threshold spectroscopy, starting with a team at Northwestern University principally consisting of my first doctoral student W. Peatman and my two outstanding, then post-doctoral associates T. Baer and P. M. Guyon.

I want to thank Professor David Buckingham, the Chairman of the Linnett Trust, for inviting me to give these lectures from which this book developed. I also want to thank the Master of Sidney-Sussex College, Professor Gabriel Horn, for his kind hospitality during my tenure of a fellowship at Sidney-Sussex.

This book is dedicated to the memory of Professor John Wilfred Linnett, professor of physical chemistry, master of Sidney-Sussex College and Vice-Chancellor of Cambridge University. It is hoped that this short primer will provide much of that which Professor Linnett provided in his two introductory texts on quantum mechanics, namely a useful first guide to students starting in a new field.