HANDBOOK OF HIGH-RESOLUTION SPECTROSCOPY

Fundamentals and Theory

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Preface

Science is built upon facts, as a house is built of stones; but an accumulation of facts is no more a science than a heap of stones is a house.

Henri Poincaré (from *Science and Hypothesis*)

Spectroscopy is probably the single most successful experimental tool in the natural sciences in a very broad sense, and the same is true for the more specifically defined field of molecular science. In particular, high-resolution molecular spectroscopy is unique in providing vast amounts of information of the highest precision and accuracy (in a quantitative sense as well as in terms of exceptional quality). However, its success also contains the germ of a defeat: All too easily, the promise of new knowledge is lost in the overwhelming amount of information.

It is thus necessary, every once in a while, to sit back and put structure and order into this field of science. This task had been accomplished during the twentieth century in an unparalleled way by the series of books by Gerhard Herzberg on atomic and molecular spectroscopy, which appeared over a period of three decades between 1936 and 1966 if one includes the original first German editions. Since the publication of the third volume of Herzberg's books on molecular spectroscopy in 1966, the series has been complemented by a systematic collection of data on diatomic molecules by Huber and Herzberg (1979). The books continued to be reprinted with minor corrections and additions until almost the end of the last century.

After 1966, however, there were important developments not included in Herzberg's books which led to a true renaissance of the field of molecular spectroscopy. We highlight, in particular, the development of the laser and the techniques of laser spectroscopy with either high frequency or high time resolution. Fourier transform spectroscopy was another important experimental development in part enabled by new computer technology in this period. In addition, quantum mechanical theory and, in particular, ab initio quantum chemistry has profited from the parallel revolution in computers over the last few decades. All these developments were of particular importance for spectroscopic studies at high resolution. It is fair to say that high-resolution molecular spectroscopy has been redefined by the new experimental and theoretical possibilities. It is now a new, very young, vigorous, and rapidly developing field in comparison to the spectroscopy of the mid-twentieth century.

Another exciting development in recent decades is the renewed interaction of high-resolution spectroscopy with the most recent evolution of fundamental physics; this interaction offers the potential for spectroscopy to make as significant contributions to science at the start of the twenty-first century as at the start of the twentieth century.

It seemed, therefore, timely to provide an up-to-date and structured summary of the status of the field. While there are many textbooks covering recent developments, including excellent books, indeed, these are either directed with a mostly didactic goal at a readership of undergraduate students or else they cover some more specialized subfield in greater depth at a research level. This has led to a somewhat fragmented coverage of the field in the literature, and a book covering the field as a whole is lacking. As no spectroscopist today can claim an encyclopedic knowledge of the entire field, the approach of the editors of the present handbook has been to invite internationally renowned scientists to provide articles covering their field of research. The present handbook is the first comprehensive survey of this area of science since Herzberg's classic books. While still certainly incomplete, we hope to correct omissions and to fill gaps in future editions.

Because of the importance of the interaction of spectroscopic experiment with theory, the handbook covers both aspects in a balanced way. After several introductory articles covering the various branches of spectroscopy (these articles should also serve a didactic purpose for courses on the topic) which include an article on conventions, nomenclature, as well as extensive tables of fundamental quantities and constants, the first volume of the handbook covers the development of theory and ab initio quantum chemistry as related to spectroscopy. In the second volume, all areas of experimental spectroscopy (microwave, infrared, visible, and ultraviolet) are covered in a systematic way. Finally, Volume 3 includes special techniques for new developments and applications in various areas of high-resolution spectroscopy. All articles were refereed and revised or edited as needed, however without too much stress on conformity. Thus the individual chapters have

retained largely their character as defined by the authors. Cross references to related articles were added throughout upon editing, to facilitate the reader's access to the various themes.

We hope that this handbook will serve advanced students, teachers, and researchers alike in their work in this exciting field of science and in doing this we hope that the book will contribute to the development of the field. We are grateful to all authors for their important contributions and to the members of our research groups who helped in many ways, particularly, Irène Müller and Ruth Schüpbach. Thanks are also due to the staff of Wiley for their continuous encouragement as well as to our wives for their support and patience during the period of preparation of this handbook.

Frédéric Merkt and Martin Quack
Zurich, July 2010