Electronic and Photoelectron Spectroscopy

Fundamentals and Case Studies

Electronic and photoelectron spectroscopy can provide extraordinarily detailed information on the properties of molecules and are in widespread use in the physical and chemical sciences. Applications extend beyond spectroscopy into important areas such as chemical dynamics, kinetics, and atmospheric chemistry. This book provides the reader with a firm grounding in the basic principles and experimental techniques employed. The extensive use of case studies effectively illustrates how spectra are assigned and how information can be extracted, communicating the matter in a compelling and instructive manner.

Topics covered include laser-induced fluorescence, resonance-enhanced multiphoton ionization, cavity ringdown and ZEKE spectroscopy. The book is for advanced undergraduate and graduate students taking courses in spectroscopy and will also be of use to anyone encountering electronic or photoelectron spectroscopy during their research.

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Preface

Modern spectroscopic techniques such as laser-induced fluorescence, resonance-enhanced multiphoton ionization (REMPI), cavity ringdown, and ZEKE are important tools in the physical and chemical sciences. These, and other techniques in electronic and photoelectron spectroscopy, can provide extraordinarily detailed information on the properties of molecules in the gas phase and see widespread use in laboratories across the world. Applications extend beyond spectroscopy into important areas such as chemical dynamics, kinetics, and analysis of complicated chemical systems such as plasmas and the Earth's atmosphere. This book aims to provide the reader with a firm grounding in the basic principles and experimental techniques employed in modern electronic and photoelectron spectroscopy. It is aimed particularly at advanced undergraduate and graduate level students studying courses in spectroscopy. However, we hope it will also be more broadly useful for the many graduate students in physical chemistry, theoretical chemistry, and chemical physics who encounter electronic and/or photoelectron spectroscopy at some point during their research and who wish to find out more.

There are already many books available describing the principles, experimental techniques, and applications of spectroscopy. However, our aim has been to produce a book that tackles the subject in a rather different way from predecessors. Students at the advanced undergraduate and early graduate levels should be in a position to develop their knowledge and understanding of spectroscopy through contact with the research literature. This has the benefit of introducing the students to the cutting edge of modern spectroscopic work and can provide insight into the thought processes involved in spectral assignment and interpretation. However, the spectroscopic research literature can initially prove daunting even to the most committed and able of students because of the range of prior knowledge assumed, the brevity of explanations, and the extensive use of jargon.

We felt that there would be benefit in taking a number of focussed, and mostly modern, research studies and presenting them in a form that is palatable for the newcomer to advanced spectroscopy. We have called these mini-chapters Case Studies and they form the heart of this book. In essence we have taken original research findings, often directly from research papers, and describe selected aspects of them in a way which not only shows the original data and conclusions, but also tries to guide the reader step-by-step through the assignment and interpretation process. In other words, we have in many cases tried to put the reader in the shoes of the research team that first recorded the spectrum or spectra, and then tried to show them *how* the spectrum was assigned.

Jargon cannot be avoided entirely – indeed it is an essential part of the language of modern spectroscopy – but we have attempted to define any specialized jargon that does arise as we encounter it.

Of course some basic background knowledge is essential before encountering more advanced concepts, and so the first two parts describe some of the principles and experimental techniques employed in modern electronic and photoelectron spectroscopy. These two parts are not intended to be exhaustive, but rather contain the basic tools necessary for delving into the Case Studies. Some of the more advanced concepts met in spectroscopy, such as vibronic coupling, nuclear spin statistics, and Hund's coupling cases, are met only in certain specific Case Studies and can be entirely avoided by the reader if desired.

As much as possible, we have tried to make the majority of the Case Studies independent. This means that the reader can dip into only those that interest him/her. At the same time, this approach inevitably leads to some repetition of material but we consider this an acceptable price to pay for producing a book in this style.

We view the Case Studies as a useful bridge between traditional teaching and fully independent learning through the research level literature. We do not in any way claim to have covered all of the important topics in modern electronic spectroscopy, nor have we attempted to treat any particular topic in great depth. However, we believe that most of the material in electronic spectroscopy encountered in advanced undergraduate and early graduate level spectroscopy courses is covered within this book. Furthermore, we hope that the focus on research material will give the reader a flavour of the kind of work that currently takes place in the spectroscopic community and will encourage him/her to explore new avenues. Whether we have been successful or not is purely for the reader to judge.

Finally, the authors would like to take this opportunity to thank Cambridge University Press for showing great patience on the numerous occasions when the finishing date for the manuscript was postponed!

Journal abbreviations

Abbreviations are used for journal titles in the list of references at the end of each chapter. The full title of each journal is listed below.

Angew. Chemie Int. Edn.	*Angewandte Chemie, International Edition in English*
Ber. Bunsenges. Phys. Chem.	*Berichte der Bunsengesellschaft für Physikalische Chemie*
Chem. Phys.	*Chemical Physics*
Chem. Phys. Lett.	*Chemical Physics Letters*
Chem. Rev.	*Chemical Reviews*
Comput. Phys. Commun.	*Computer Physics Communications*
Found. Phys.	*Foundations of Physics*
Instrum. Sci. Technol.	*Instrumentation Science and Technology*
Int. Rev. Phys. Chem.	*International Reviews in Physical Chemistry*
J. Chem. Educ.	*Journal of Chemical Education*
J. Chem. Phys.	*Journal of Chemical Physics*
J. Chem. Soc.	*Journal of the Chemical Society*
J. Electron Spectrosc. Rel. Phenom.	*Journal of Electron Spectroscopy and Related Phenomena*
J. Mol. Spectrosc.	*Journal of Molecular Spectroscopy*
J. Opt. Soc. Am.	*Journal of the Optical Society of America*
J. Phys. Chem.	*Journal of Physical Chemistry*
Math. Comp.	*Mathematics of Computation*
Mol. Phys.	*Molecular Physics*
Philos. Trans. Roy. Soc.	*Philosophical Transactions of the Royal Society of London*
Phys. Rev.	*Physical Review*
Vib. Spectrosc.	*Vibrational Spectroscopy*
Z. Phys.	*Zeitschrift für Physik*
Z. Wiss. Photogr. Photophys. Photochem.	*Zeitschift für Wissenschaftliche Photographie, photophysik und photochemie*