# Atomic and Molecular Spectroscopy

**Basic Concepts and Applications** 

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> To my father Late Shri Om Prakash Chadha

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### Preface

This book is primarily intended for post-graduate students of science, but is simple enough for an undergraduate student to understand. Every chapter begins with simple concepts related to the topic of the chapter, and gradually Quantum Mechanical and Group Theoretical treatments are introduced for a deeper understanding. I have tried to keep the language simple and have introduced new concepts one at a time, so that the reader is not overwhelmed by too many new ideas at the same time.

Spectroscopy is so vast and new concepts are rapidly emerging, so that it is not possible for a book to be complete. This book does not pretend to be complete—but it does try to cover the underlying principles thoroughly so that the reader should not face difficulty in applying these principles to his own problem.

Spectroscopy cannot be understood without a thorough knowledge and understanding of quantum mechanics. Though a number of Quantum Mechanics principles are scattered throughout the book, the reader is advised to first take at least an elementary course on quantum mechanics. The reader must also familiarize himself/herself with Group Theory—at least to the extent of assignment of molecular point groups, calculation of direct products, projection operator techniques, etc. There are a number of excellent texts, namely Cotton, Schonland, Ladd, to name a few. Again, a brief description of these techniques is given as and when required. Though I was advised by a reviewer of the book to include a chapter on Group Theory, it would have added to the volume and cost of the book, because there is nothing I could have removed from the other chapters in order to keep the page number around 400.

One other point—all chapters are arranged in sequence, so that a concept introduced in a certain chapter is used in one of the next chapters—so you cannot expect to understand, say the third chapter, without first reading the first two chapters. I have spent a lot of thought on the arrangement of the chapters—in the short time of one semester, it is extremely important that everything is taught without any repetition. In this respect, though in most books atomic spectroscopy is taught along with electronic spectroscopy, in this book it is the first topic to be covered. The reason is the simplicity of atomic spectroscopy, which has no complications from rotation and vibration, as in the case of molecular electronic spectroscopy. The entire sequence may be different from other books, but in my experience this is the only way I am able to cover the entire syllabus (which also includes NMR and Mössbauer spectroscopy and X-ray diffraction) in 50 hours. After a lot of jugglery during the initial years of teaching the paper, this is the sequence that I found to serve my purpose.

#### xviii Preface

A motivation for writing the book was that, although several excellent books exist on the subject (Banwell, Hollas, Barrow, Chang, to name a few), no single book covers all the topics I wished to include. Many of the texts are also outdated. The level of this book is all the way from Banwell to Hollas and more. The symbols and units used in the book are in conformity with those recommended by IUPAC.

Though every possible effort has been made to avoid errors, in a project of this size, it is inevitable that some errors may have crept in. I shall be thankful to readers if they point them out so that future editions will be error free. Any suggestion or constructive criticism will be highly appreciated.

Rita Kakkar, FRSC

### Acknowledgements

This is the best part of the book where I can pen my thoughts without worrying about scientific accuracy. I owe this book to all those who directly or indirectly encouraged me. My first source of motivation was the thousands of students who thronged my spectroscopy class. There can be no better encouragement than the rapt attention of these young souls, their inquisitive questions, coming to me with their doubts after class, their excitement at scoring well in the paper, coming after the NET (National eligibility test) and telling me that they were successful in "cracking" it because of their understanding of spectroscopy and quantum mechanics. For all these students, many of whom have told me that they use my class-notes even for undergraduate teaching, I have brought out this book. As all teachers would agree, there is no satisfaction greater than the high one gets after a well-appreciated class.

To my research group of nearly 40 students, past and present, I owe a lot of thanks for constantly encouraging me to write the book. They are now urging me to write another book on quantum mechanics! To the present lot of students, who had to wait for me to get free from the book before I could check their research papers, thank you for your patience!

I am indebted to all my teachers who made learning fun. I was fortunate to be taught by some of the best teachers, both during my undergraduate and postgraduate studies. For spectroscopy, especially, I was fortunate to be taught by the likes of the late Professors N. K. Ray and V. M. Khanna. Professor N. K. Ray had the knack to make complex quantum mechanics seem so simple, while Professor V. M. Khanna's mastery of spectroscopy was phenomenal. His problem sets were unique and I have included some of his questions in the book. I was also fortunate to have taught three core courses—quantum mechanics, statistical thermodynamics and spectroscopy—in parallel with him and am indebted to him for his guidance. I would also specially mention Professor J. Nagchaudhuri. I do not know where she is at present, but when she left for Kolkata after retirement, she promised to write a book on spectroscopy and remain in touch. That was before the time of the internet and e-mail, and we somehow lost touch. While Professor V. M. Khanna was adept at the theoretical aspects of spectroscopy, she also brought in the experimental aspects. Teaching alongside her, I learnt to include some experimental topics in my teaching. The result is a nice amalgamation of theoretical and experimental spectroscopy, and I sincerely hope that it will be appreciated.

To my publisher's representative, Mr. Gauravjeet Reen of Cambridge University Press, thank you for extending the deadline and your understanding. This soft-spoken gentleman would call me telephonically and ask politely whether this was a good time to talk, and then throw a bombshell by advancing the date of submission of the manuscript. This kept me on my

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toes. Finally, when the deadline approached, he told me to take my own time, saving me from more sleepless nights.

The acknowledgements would not be complete if I did not appreciate the anonymous reviewers of the book, both national and international. Their comments have definitely helped. I particularly thank one reviewer for suggesting an easy to remember expression for the moment of inertia of linear polyatomic molecules, which I have included in the text. That brings me to my son, Chetan. He was studying in Class IX when I was writing the Rotational Spectroscopy chapter and he just happened to pass by my computer. He asked me why I was deriving the expression for OCS in such a complicated way, when the parallel axis theorem (which he was studying in Physics then) could be used, and I included his derivation in the book.

I dedicate the book to my parents—my late father who always had faith in me and my mother for her excellent advice at all times, her commitment to education—she was a graduate in Economics at a time when women hardly studied. At the age of 90+, she still remembered the poetry we learnt at school and have forgotten. She would advise her children and grand children (from Longfellow's *A Psalm of Life*) "*Be not like dumb, driven cattle! Be a hero in the strife*". Unfortunately, she passed away during production of the book. Without my parents' constant support, I would not have been what I am today. I cannot thank my Dad enough for his support. On looking at my notes, I came across his hand-writing. In my graduation days, our Department library had just one copy of Banwell (the cheap Indian edition had not been published then) and it was issued to students just for a day. Photostat was not so common then, and he actually copied some of the pages for me. I also owe my love for mathematics to him—though I am not as quick as him at doing arithmetic in my head.

Last, but not the least, I would like to express my heartfelt gratitude to my immediate family for putting up with me and my erratic hours during writing of the book. A special word of thanks to my husband, Dr. Subhash Kakkar, for his constant support through thick and thin. To my son Chetan, thank you for making life worth living. Besides the emotional support that the two have provided, both of them have also helped in the preparation of the manuscript—my husband by encouraging me to draw the figures myself, starting by drawing a few of those himself, and my son by providing technical help and advice throughout, the computer wizard that he is.

Rita Kakkar, FRSC

# **List of Abbreviations**

NMR	Nuclear Magnetic Resonance
ESR	Electron Spin Resonance
UV	Ultraviolet
IR	Infrared
MW	Microwave
FWHM	Full Width at Half Maximum
Vis	Visible
FT	Fourier Transform
FFT	Fast Fourier Transform
QM	Quantum Mechanics
PES	Photoelectron Spectroscopy
ESCA	Electron Spectroscopy for Chemical Analysis
XPS	X-ray Photoelectron Spectroscopy
IE	Ionization Energy
СОМ	Centre of Mass
MO	Molecular Orbital
НОМО	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
HMO	Hückel Molecular Orbital
FEM	Free Electron Model
ISC	Intersystem Crossing
VR	Vibrational Relaxation
IC	Internal Conversion
AO	Atomic Orbital
rms	Root Mean Square
LCAO	Linear Combination of Atomic Orbitals