

## Rotational Spectroscopy of Diatomic Molecules

Written to be the definitive text on the rotational spectroscopy of diatomic molecules, this book develops the theory behind the energy levels of diatomic molecules and then summarises the many experimental methods used to study the spectra of these molecules in the gaseous state.

After a general introduction, the methods used to separate nuclear and electronic motions are described. Brown and Carrington then show how the fundamental Dirac and Breit equations may be developed to provide comprehensive descriptions of the kinetic and potential energy terms which govern the behaviour of the electrons. One chapter is devoted solely to angular momentum theory and another describes the development of the so-called effective Hamiltonian used to analyse and understand the experimental spectra of diatomic molecules. The remainder of the book concentrates on experimental methods.

This book will be of interest to graduate students and researchers interested in the rotational spectroscopy of diatomic molecules.

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# Rotational Spectroscopy of Diatomic Molecules

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## Preface

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A book whose title refers to the spectroscopy of diatomic molecules is, inevitably, going to be compared with the classic book written by G. Herzberg under the title *Spectroscopy of Diatomic Molecules*. This book was published in 1950, and it dealt almost entirely with electronic spectroscopy in the gas phase, studied by the classic spectrographic techniques employing photographic plates. The spectroscopic resolution at that time was limited to around  $0.1\text{ cm}^{-1}$  by the Doppler effect; this meant that the vibrational and rotational structure of electronic absorption or emission band systems could be easily resolved in most systems. The diatomic molecules studied by 1950 included conventional closed shell systems, and a large number of open shell electronic states of molecules in both their ground and excited states. Herzberg presented a beautiful and detailed summary of the principles underlying the analysis of such spectra. The theory of the rotational levels of both closed and open shell diatomic molecules was already well developed by 1950, and the correlation of experimental and theoretical results was one of the major achievements of Herzberg's book. It is a matter of deep regret to us both that we cannot present our book to 'GH' for, hopefully, his approval. On the other hand, we were both privileged to spend time working in the laboratory in Ottawa directed by GH, and to have known him as a colleague, mentor and friend.

Accepting, therefore, the possible and perhaps likely comparison with Herzberg's book, we should say at the outset that almost everything described in our book relates to work published after 1950, and the philosophy and approach of our book is different from that of Herzberg, as it surely should be over 50 years on. The Doppler width of  $0.1\text{ cm}^{-1}$  characteristic of conventional visible and ultraviolet electronic spectra, corresponding to 3000 MHz in frequency units, conceals much of what is most interesting and fundamental to the spectroscopic and electronic properties of diatomic molecules. Our book deals with the experimental and theoretical study of these details, revealed by measurement of either transitions *between* rotational levels, or transitions *within* a single rotational level, occurring between the fine or hyperfine components. This branch of spectroscopy is often called rotational spectroscopy, and it involves much lower frequency regions of the electromagnetic spectrum than those arising in conventional electronic or vibrational spectroscopy. The experimental work described in this book ranges from the far-infrared, through the microwave, to the radiofrequency regions of

the spectrum; the intrinsic Doppler width is small because of the lower frequency, and special techniques, particularly those involving molecular beams, sometimes result in very high spectroscopic resolution. Molecules in open shell electronic states possess a number of subtle intramolecular magnetic and electric interactions, revealed by these high-resolution studies. Additional studies involving the effects of applied magnetic or electric fields provide further information, particularly about electron and nuclear spin magnetic moments. All of the experimental work described in this book involves molecules in the gas phase. Consequently we include descriptions of conventional microwave and millimetre wave rotational spectroscopy, subjects which would be familiar to most molecular spectroscopists. However, we give equal prominence to the molecular beam magnetic resonance studies of the small magnetic interactions arising from the presence of magnetic nuclei in closed shell molecules. These classic studies formed the basis for subsequent nuclear magnetic resonance studies of condensed phases; similarly the magnetic interactions studied through condensed phase electron spin resonance experiments were first understood through high-resolution gas phase investigations described in this book. These are subjects which, more often than not, do not appear in the same book as rotational spectroscopy, but they should.

The important threads which link these different branches of gas phase rotational spectroscopy are, of course, those arising from the theory. We have tried to make clear the distinction between two different types of theory. A spectroscopist analyses a spectrum by using algebraic expressions for transition frequencies which involve appropriate quantum numbers and ‘molecular constants’. These expressions arise from the use of an *effective* Hamiltonian, which summarises the relevant intramolecular dynamics and interactions, and is expressed in terms of molecular parameters and operators, usually angular momentum operators. A central theme of our book is the construction and use of the effective Hamiltonian, and through it some more precise definitions of the molecular constants or parameters. We show, at length, how the effective Hamiltonian is derived from a consideration of the fundamental *true* Hamiltonian, although the word ‘true’ must be used with caution and some respect. We take as our foundations the Dirac equation for one electron, and the Breit equation for two electrons. We show how the ‘true’ Hamiltonian for a molecule, in the presence of external fields, is derived, and show how this may be applied to the derivation of an ‘effective’ Hamiltonian appropriate for any particular molecular system or spectroscopic study. We have made a compromise in our analysis; we do not delve into quantum electrodynamics! One of the lessons in the life of a serious spectroscopist is that there is always a level of understanding deeper than that being employed, and we all have to compromise somewhere.

Chapters 2 to 7 deal with the essentials of the theory, starting with the separation of nuclear and electronic motion, and finishing with the derivation of effective Hamiltonians. An important aspect of diatomic molecules is their high symmetry, and the various angular momenta which can arise. Angular momentum theory is summarised in chapter 5 where we show the importance of rotational symmetry by introducing spherical tensors to describe the angular momenta and their interactions, both with each other and with applied fields. Spherical tensor methods are used throughout



the book; we have used them to describe the analysis of particular spectra even if the original work used cartesian tensors. Spherical tensor, or irreducible tensor methods bring out the links between different parts of the subject; they make maximum use of symmetry and, to our minds at least, are simpler and more reliable in their use than the older cartesian methods. This is particularly true of problems which involve transformations from space to molecule-fixed axes, for example, the effects of applied magnetic or electric fields.

Chapters 8 to 11 describe the details and results of experimental studies. Chapter 8 deals with molecular beam magnetic and electric resonance, chapter 9 with magnetic resonance of open shell molecules in the bulk gas phase, chapter 10 with pure rotational spectroscopy in the bulk gas phase, and chapter 11 with double resonance studies. Of course, these topics overlap and some molecules, the OH radical for example, appear in all four chapters. We have deliberately allowed some repetition in our discussion, because in the process of following a complicated analysis, it is very annoying to be forced to jump to other parts of a book for some essential details. Our overriding philosophy has been to choose particularly important examples which illustrate the details for particular types of electronic state, and to work through the theory and analysis in considerable detail. Although there is a substantial amount of experimental data in our book, we have not intended to be comprehensive in this respect. Computerised data bases, and the various encyclopaedic assemblies are the places to seek for data on specific molecules. As mentioned earlier, we have analysed the experimental data using spherical tensor methods, even if the original work used cartesian methods, as was often the case with the earlier studies.

The question of units always poses a problem for anyone writing a book in our field. Most authors from North America use cgs units, and most of the work described in this book originated in the USA. Authors from the UK and Europe, on the other hand, have largely been converted to using SI units. There is no doubt that the SI system is the more logical, and that numerical calculations using SI units are more easily accomplished. Nevertheless since so many spectra are still assigned and analysed using cgs units, we have had to seek a compromise solution. The fundamental theory describing the electronic Hamiltonian, presented in chapter 3, uses SI units. Similarly we use SI units in describing the theory of nuclear hyperfine interactions in chapter 4. However, chapters 8 to 11, which deal with the analysis of spectra, are written in terms of both cgs and SI units, so that direct comparisons with the original literature can be made. A comparison of the cgs and SI units is presented in General Appendix D. To complicate matters even further, the use of *atomic* units, which is common in *ab initio* electronic structure calculations because of the simplifications introduced, is described in chapter 6.

The gestation period for this book has been particularly long, work on it having started around 1970 when we were both members of the Department of Chemistry at Southampton University. Research was going rather slowly at the time and we had a keen desire to understand the foundations of our subject properly. We worked through the various aspects together, and put the material in writing. At first we had only the other members of the group in mind but, as things developed, we started to write for a

wider audience. We were encouraged and greatly helped at the time by our colleague, Dr Richard Moss, who gave an outstanding post-graduate course on relativistic quantum mechanics. Chapters 2, 3 and 4 of the present book were essentially written at that time. The writing process, however, eventually gave way to other things, particularly research, and it seemed that the unfinished book, like so many others, was destined for the scrap heap. There it remained until one of us (AC), conscious of approaching enforced 'retirement', decided to revive the project as an antidote to possible vegetation. The dusty old manuscript was scanned into a computer, revised, and over a period of four years developed into the book now published. The passage of some thirty years between the two phases of writing has undoubtedly had some benefits. In particular, it has allowed the time for important new technical developments to take place, and for the subject (and the authors) to mature generally.

The manuscript for this book was produced using MSWord text and equation editor, with MATHTYPE used to control equation numbering and cross-referencing. Those figures which include an experimental spectrum were produced using SigmaPlot, each spectrum being obtained in XY array form by a digitising scan of the original paper. All other figures were produced using CoralDraw.

We are grateful to several friends and colleagues who have read parts of the book and given us their comments. In particular we thank Professors B.J. Howard, T.A. Miller, T.C. Steimle, M. McCarthy, M.S. Child and Dr I.R. McNab. We will always be glad to receive comments from readers, kind, helpful, or otherwise! Alan Carrington would like to thank the Leverhulme Trust for an Emeritus Fellowship which has enabled him to keep in close touch with the subject through attendances at conferences.

This book is dedicated to the memory of Bill Flygare, Harry Radford and Ken Evenson.

Alan Carrington  
John M. Brown  
April 2002

## Summary of notation

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Throughout this book we have used, at different times, space-fixed or molecule-fixed axis systems, with arbitrary origin, origin at the molecular centre of mass, origin at the nuclear centre of mass, or origin at the geometrical centre of the nuclei. We use CAPITAL letters for SPACE-FIXED axes, and lower case letters for molecule-fixed axes. The various origins are denoted by primes as follows.

- (i) Space-fixed axes: arbitrary origin.

$\mathbf{R}_\alpha$  = position vector of nucleus  $\alpha$

$\mathbf{P}_\alpha$  = momentum conjugate to  $\mathbf{R}_\alpha$

$\mathbf{R}_i$  = position vector of  $i$ th electron

$\mathbf{P}_i$  = momentum conjugate to  $\mathbf{R}_i$

$\mathbf{S}_i$  = spin of  $i$ th electron

$X, Y, Z$  = space-fixed axes

- (ii) Space-fixed axes: origin at molecular centre of mass.

$\mathbf{R}'_\alpha, \mathbf{P}'_\alpha, \mathbf{R}'_i, \mathbf{P}'_i$ , defined by analogy with  $\mathbf{R}_\alpha$ , etc.,

$\mathbf{R}_O$  = position vector of molecular centre of mass with respect to the arbitrary origin

$\mathbf{P}_O$  = momentum conjugate to  $\mathbf{R}_O$ , i.e., translational momentum

$\mathbf{R}$  = internuclear vector =  $\mathbf{R}_2 - \mathbf{R}_1 = \mathbf{R}'_2 - \mathbf{R}'_1$

$\mathbf{S}_i$  = spin of  $i$ th electron

- (iii) Space-fixed axes: origin at nuclear centre of mass.

$\mathbf{P}''_\alpha, \mathbf{R}''_\alpha, \mathbf{P}''_i, \mathbf{R}''_i, \mathbf{R}, \mathbf{S}_i$

- (iv) Space-fixed axes: origin at geometrical centre of nuclei.

$\mathbf{P}'''_\alpha, \mathbf{R}'''_\alpha, \mathbf{P}'''_i, \mathbf{R}'''_i$

- (v) Molecule-fixed axes: origin at nuclear centre of mass.

$\mathbf{r}_i, \mathbf{p}_i, \mathbf{S}_i$

When dealing with components of vector quantities we usually use subscripts  $X, Y, Z$  or  $x, y, z$  for space-fixed or molecule-fixed components, the origin of coordinates usually being denoted in the primary subscripted symbol. For the electron spin we use capital  $\mathbf{S}_i$  for space-fixed axes and small  $s_i$  for molecule-fixed; it is not necessary to distinguish the origin of coordinates. A difficulty with this notation is that, in conformity with common practice, we also use the symbol  $\mathbf{S}$  to denote the total spin ( $\Sigma_i s_i$  or  $\Sigma_i \mathbf{S}_i$ ). We hope

to avoid confusion in the appropriate text. We use  $M$  or  $M_s$  to denote the component of  $S$  in the space-fixed  $Z$  direction, and  $m$  or  $m_s$  to denote the component of  $s$  in the molecule-fixed  $z$  direction, i.e. along the internuclear axis. We shall also sometimes use  $\Sigma$  to denote  $m_s$ . Hence  $\psi_M$  denotes a spinor in the space-fixed axis system and  $\psi_m$  refers to the molecule-fixed axes.

Other symbols used are as follows:

- $i', j', k'$  = unit vectors along  $X, Y, Z$
- $i, j, k$  = unit vectors along  $x, y, z$
- $\varepsilon_i$  = electric field strength at electron  $i$  arising from other electrons and nuclei
- $E_i$  = applied electric field strength at electron  $i$
- $B_i$  = applied magnetic flux density at electron  $i$
- $A_i$  = total magnetic vector potential at electron  $i$
- $A_i^e$  = contribution to  $A_i$  from other electrons
- $A_i^B$  = contribution to  $A_i$  from external magnetic field
- $\phi_i$  = total electric potential at electron  $i$
- $A_\alpha$  = total magnetic vector potential at nucleus  $\alpha$
- $A_\alpha^e$  = contribution to  $A_\alpha$  from electrons
- $A_\alpha^B$  = contribution to  $A_\alpha$  from external magnetic field
- $\phi_\alpha$  = total electric potential at nucleus  $\alpha$
- $B_\alpha$  = applied magnetic flux density at nucleus  $\alpha$
- $E_\alpha$  = applied electric field strength at nucleus  $\alpha$
- $B = B_i = B_\alpha$  for homogeneous magnetic field
- $E = E_i = E_\alpha$  for homogeneous electric field
- $\Lambda$  = projection of  $L$  along internuclear axis
- $\Sigma, m_s$  = projection of  $S$  along internuclear axis
- $\Omega = |\Lambda + \Sigma|$  = projection of total electronic angular momentum along internuclear axis
- $\mathcal{D}_{M,m}^{(1/2)}(\phi, \theta, \chi)$  = rotational matrix for spin transformation
- $V$  or  $v$  = classical velocity vector
- $\mathcal{L}$  = Lagrangian
- $E$  = energy
- $t$  = time
- $\sigma'$  = Pauli spin vector
- $\sigma$  = Dirac spin vector
- $\mu_S$  = electron spin magnetic moment
- $\mu_I$  = nuclear spin magnetic moment
- $\mu_r$  or  $\mu_J$  = rotational magnetic moment
- $\mu_e$  = electric dipole moment
- $\bar{S}$  = Foldy–Wouthuysen operator
- $\nabla$  = gradient operator
- $\nabla^2$  = Laplacian
- $\delta()$  = Dirac delta function

- $\pi$  = pi, 3.141 592 653...  
 $M_\alpha$  = mass of nucleus  $\alpha$   
 $m_i$  (or  $m$ ) = mass of electron  
 $M_p$  = proton mass  
 $\mu$  = reduced nuclear mass (possible confusion here with magnetic moment)  
 $\mu_\alpha = M_1 M_2 / (M_1 + M_2)$   
 $M$  = total molecular mass  
 $h$  = the Planck constant  
 $\hbar = h/2\pi$   
 $\mu_B$  = electron Bohr magneton =  $e\hbar/2m$   
 $\mu_N$  = nuclear Bohr magneton =  $e\hbar/2M_p$   
 $c$  = speed of light  
 $e$  = elementary unit of charge (defined to be positive)  
 $-e$  = electron charge  
 $Z_\alpha e$  = nuclear charge  
 $\alpha, \beta$  denote  $m_s$  or  $M_s = +1/2, -1/2$   
 $\pi$  = mechanical momentum in presence of electromagnetic fields  
 $\alpha$  = Dirac momentum operator  
 $\beta$  = Dirac matrix  
 $L$  = orbital angular momentum  
 $S$  = electron spin angular momentum  
 $P$  = total electronic angular momentum  
 $J$  = total angular momentum excluding nuclear spin  
 $N$  = total angular momentum excluding electron and nuclear spin  
 $R$  = rotational angular momentum of the bare nuclei  
 $I$  = nuclear spin angular momentum  
 $F$  = grand total angular momentum including electron and nuclear spin  
 $R$  = internuclear distance  
 $\phi, \theta, \chi$  = Euler angles  
 $\bar{R}$  = mean position operator in the Dirac representation  
 $R''$  = position operator in the F–W representation (confusion)  
 $I_\alpha$  = spin of nucleus  $\alpha$   
 $g_S$  = electron  $g$  factor: value = 2 in the Dirac theory, 2.002 32 from quantum electrodynamics  
 $g_N$  = nuclear  $g$  factor  
 $g_L$  = orbital  $g$  factor  
 $g_r$  or  $g_J$  = rotational  $g$ -factor  
 $i = \sqrt{-1}$

### Some additional notes

Vector quantities are denoted by bold font. Although the square of a vector, i.e. the scalar product of the vector with itself, is a scalar quantity, we have followed the commonest convention of also denoting the vector squares in bold font.

An applied magnetic field is denoted  $B_Z$  throughout this book; we use the alternative  $B_0$ , to denote the rotational constant for the  $v = 0$  level.

Additional molecular parameters which arise in effective Hamiltonians are listed in Appendix 7.1.

## Figure acknowledgements

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The figures in this book are of two different types. Figures which are solely line drawings were produced using CoralDraw; in some cases the drawings are similar to figures published elsewhere, and appropriate acknowledgements are given below. Other figures contain reproductions of experimentally recorded spectra. In these cases the literature spectrum was first photocopied, and the copy then digitally scanned to produce the data in the form of a numerical XY array. The spectrum was regenerated from the XY array using SigmaPlot, and appropriate annotation added as required. Acknowledgements to the original sources of the spectra are listed below.

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