MODERN SPECTROSCOPY

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Preface

Modern Spectroscopy has been written to fulfil a need for an up-to-date text on spectroscopy. It is aimed primarily at a typical undergraduate audience in chemistry, chemical physics, or physics in the United Kingdom and at both undergraduate and graduate student audiences elsewhere.

Spectroscopy covers a very wide area which has been widened further since the mid-1960s by the development of lasers and such techniques as photoelectron spectroscopy and other closely related spectroscopies. The importance of spectroscopy in the physical and chemical processes going on in planets, stars, comets, and the interstellar medium has continued to grow as a result of the use of satellites and the building of radiotelescopes for the microwave and millimetre wave regions.

In planning a book of this type I encountered three major problems. The first is that of covering the analytical as well as the more fundamental aspects of the subject. The importance of the applications of spectroscopy to analytical chemistry cannot be overstated but the use of many of the available techniques does not necessarily require a detailed understanding of the processes involved. I have tried to refer to experimental methods and analytical applications where relevant.

The second problem relates to the inclusion, or otherwise, of molecular symmetry arguments. There is no avoiding the fact that an understanding of molecular symmetry presents a hurdle (although I think it is a low one) which must be surmounted if selection rules in vibrational and electronic spectroscopy of polyatomic molecules are to be understood. This book surmounts the hurdle in Chapter 4 which is devoted to molecular symmetry but which treats the subject in a non-mathematical way. For those lecturers and students who wish to leave out this chapter much of the subsequent material can be understood but, in some areas, in a less satisfying way.

The third problem also concerns the choice of whether to leave out certain material. In a book of this size it is not possible to cover all branches of spectroscopy. Such decisions are difficult ones but I have chosen not to

include spin resonance spectroscopy (n.m.r. and e.s.r.), nuclear quadrupole resonance spectroscopy (n.q.r.), and Mössbauer spectroscopy. The exclusion of these areas, which have been well covered in other texts, has been caused, I suppose, by the inclusion, in Chapter 8, of photoelectron spectroscopy (ultraviolet and X-ray), Auger electron spectroscopy, and extended X-ray absorption fine structure, including applications to studies of solid surfaces, and, in Chapter 9, the theory and some examples of lasers and some of their uses in spectroscopy. Most of the material in these two chapters will not be found in comparable texts but is of very great importance in spectroscopy today.

My understanding of spectroscopy owes much to having been fortunate in working in and discussing the subject with Professor I. M. Mills, Dr. A. G. Robiette, Professor J. A. Pople, Professor D. H. Whiffen, Dr. J. K. G. Watson, Dr. G. Herzberg, Dr. A. E. Douglas, Dr. D. A. Ramsay, Professor D. P. Craig, Professor J. H. Callomon, and Professor G. W. King (in more or less reverse historical order), and I am grateful to all of them.

When my previous book *High Resolution Spectroscopy* was published by Butterworths in 1982 I had it in mind to make some of the subject matter contained in it more accessible to students at a later date. This is what I have tried to do in *Modern Spectroscopy* and I would like to express my appreciation to Butterworths for allowing me to use some textual material and, particularly, many of the figures from *High Resolution Spectroscopy*. New figures were very competently drawn by Mr. M. R. Barton.

Although I have not included *High Resolution Spectroscopy* in the bibliography of any of the chapters it is recommended as further reading on all topics.

Mr. A. R. Bacon helped greatly with the page proof reading and I would like to thank him very much for his careful work. Finally, I would like to express my sincere thanks to Mrs. A. Gillett for making such a very good job of typing the manuscript.

J. Michael Hollas

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Units, dimensions, and conventions

Throughout the book I have adhered to the SI system of units, with a few exceptions. The angstrom (Å) unit, where 1 Å = 10^{-10}m, seems to be persisting generally when quoting bond lengths, which are of the order of 1 Å. I have continued this usage but, when quoting wavelengths in the visible and near-ultraviolet regions, I have used the nanometre, where 1 nm = 10 Å. The angstrom is still used sometimes in this context but it seems just as convenient to write, say, 352.3 nm as 3523 Å.

In photoelectron and related spectroscopies ionization energies are measured. For many years such energies have been quoted in electron volts, where 1 eV = 1.602 177 38 × 10^{-19}J, and I have continued to use this unit.

Pressure measurements are not often quoted in the text but the unit of Torr, where 1 Torr = 1 mmHg = 133.322 387 Pa, is a convenient practical unit and appears occasionally.

Dimensions are physical quantities such as mass, length, and time and examples of units corresponding to these dimensions are the gram (g), metre (m), and second (s). If, for example, something has a mass of 3.5 g then we write

$$m = 3.5 \text{ g}$$

Units, here the gram, can be treated algebraically so that, if we divide both sides by 'g', we get

$$m/\text{g} = 3.5$$

The right-hand side is now a pure number and, if we wish to plot mass, in grams, against, say, volume on a graph we label the mass axis 'm/g' so that the values marked along the axis are pure numbers. Similarly, if we wish to tabulate a series of masses, we put 'm/g' at the head of a column of what are now pure numbers. The old style of using 'm(g) ' is now seen to be incorrect

as, algebraically, it could be interpreted only as $m \times g$ rather than $m \div g$ which we require.

An issue which is still only just being resolved concerns the use of the word 'wavenumber'. Whereas the frequency ν of electromagnetic radiation is related to the wavelength λ by

$$\nu = \frac{c}{\lambda}$$

where c is the speed of light, the wavenumber $\tilde{\nu}$ is simply its reciprocal:

$$\tilde{\nu} = \frac{1}{\lambda}$$

Since c has dimensions of LT^{-1} and λ those of L, frequency has dimensions of T^{-1} and often has units of s^{-1} (or hertz). On the other hand, wavenumber has dimensions of L^{-1} and often has units of cm^{-1}. Therefore

$$\nu = 15.3 \text{ s}^{-1} \text{ (or hertz)}$$

is, in words, 'the frequency is 15.3 reciprocal seconds (or second-minus-one or hertz)', and

$$\tilde{\nu} = 20.6 \text{ cm}^{-1}$$

is, in words, 'the wavenumber is 20.3 reciprocal centimetres (or centimetre-minus-one)'. All of this seems simple and straightforward but the fact is that many of us would put the second equation, in words, as 'the frequency is 20.3 wavenumbers'. This is quite illogical but very common — although not, I hope, in this book.

Another illogicality is the very common use of the symbols A, B, and C for rotational constants irrespective of whether they have dimensions of frequency or wavenumber. It is bad practice to do this, but although a few have used $\tilde{A}$, $\tilde{B}$, and $\tilde{C}$ to imply dimensions of wavenumber, this excellent idea has only rarely been put into practice and, regretfully, I go along with a very large majority and use A, B and C whatever their dimensions.

The starting points for many conventions in spectroscopy are the paper by R. S. Mulliken in the *Journal of Chemical Physics* (**23**, 1997, 1955) and the books of G. Herzberg. Apart from straightforward recommendations of symbols for physical quantities which are generally adhered to, there are rather more contentious recommendations. These include the labelling of cartesian axes in discussions of molecular symmetry and the numbering of vibrations in a polyatomic molecule which are often, but not always, used. In such cases it is important that any author makes it clear what convention *is* being used.

The case of vibrational numbering in, say, fluorobenzene illustrates the point that we must be flexible when it may be helpful. Many of the vibrations of fluorobenzene strongly resemble those of benzene. In 1934, before the Mulliken recommendations of 1955, E. B. Wilson had devised a numbering scheme for the thirty vibrations of benzene. This was so well established by 1955 that its use has tended to continue ever since. In fluorobenzene there is the further complication that, although Mulliken's system provides it with its own numbering scheme, it is useful very often to use the same number for a benzene-like vibration as it has in benzene itself — for which there is a choice of Mulliken's or Wilson's numbering! Clearly not all problems of conventions have been solved, and some are not really soluble, but we should all try to make it clear to any reader just what choice we have made.

One very useful convention which was proposed by J.C.D. Brand, J. H. Callomon, and J.K.G. Watson in 1963 is applicable to electronic spectra of polyatomic molecules, and I have used it throughout this book. In this system 32_1^2, for example, refers to a vibrational transition, in an electronic band system, from $v = 1$ in the lower to $v = 2$ in the upper electronic state where the vibration concerned is the one whose conventional number is 32. It is a very neat system compared to, for example, (001) – (100). which is still frequently used for triatomics to indicate a transition from the $v = 1$ level in ν_1 in the lower electronic state to the $v = 1$ level in ν_3 in the upper electronic state. The general symbolism in this system is $(v_1'v_2'v_3') - (v_1''v_2''v_3'')$. The alternative $3_0^1\,1_1^0$ label is much more compact but is little used for such small molecules. For consistency I have used this compact symbolism throughout.

Although it is less often done, I have used an analogous symbolism for pure vibrational transitions for the sake of consistency. Here $N_{v''}^{v'}$ refers to a vibrational (infrared or Raman) transition from a lower state with vibrational quantum number v'' to an upper state v' in the vibration numbered N.

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CHAPTER 1

Some important results in quantum mechanics

1.1 Spectroscopy and Quantum Mechanics

Spectroscopy is basically an experimental subject and is concerned with the absorption, emission, or scattering of electromagnetic radiation by atoms or molecules. As we shall see in Chapter 3, electromagnetic radiation covers a wide wavelength range from radio waves to γ-rays and the atoms or molecules may be in the gas, liquid, or solid phase or, of great importance in surface chemistry, adsorbed on a solid surface.

Quantum mechanics, on the other hand, is a theoretical subject relating to many aspects of chemistry and physics, but particularly to spectroscopy.

Experimental methods of spectroscopy began in the more accessible visible region of the electromagnetic spectrum where the eye could be used as the detector. In 1665 Newton had started his famous experiments on the dispersion of white light into a range of colours using a triangular glass prism. However it was not until about 1860 that Bunsen and Kirchhoff began to develop the prism spectroscope as an integrated unit for use as an analytical instrument. Early applications were the observation of the emission spectra of various samples in a flame, the origin of flame tests for various elements, and of the sun.

The visible spectrum of atomic hydrogen had been observed both in the solar spectrum and in an electrical discharge in molecular hydrogen many years earlier, but it was not until 1885 that Balmer fitted the resulting series of lines to a mathematical formula. In this way began the close relationship between experiment and theory in spectroscopy, the experiments providing the results and the relevant theory attempting to explain them and to predict results in related experiments. However theory ran increasingly into trouble so long as it was based on classical newtonian mechanics until, from 1926 onwards, the development by Schrödinger of quantum mechanics. Even after this breakthrough, the importance of which cannot be overstressed, it is not, I think, unfair to say that theory tended to limp along behind experiment. Data from spectroscopic experiments, except for those on the simplest atoms

and molecules, were easily able to outstrip the predictions of theory which was almost always limited by the approximations which had to be made in order that the calculations would be manageable. It was only from about 1960 onwards that the situation changed as a result of the availability of large, fast computers requiring many fewer approximations to be made. Nowadays it is not uncommon for predictions to be made of spectroscopic and structural properties of fairly small molecules which are comparable in accuracy with those obtainable from experiment.

Although spectroscopy and quantum mechanics are closely interrelated it is nevertheless the case that there is still a tendency to teach the subjects separately while drawing attention to the obvious overlap areas. This is the attitude I shall adopt in this book, which is concerned primarily with the techniques of spectroscopy and the interpretation of the data which accrue. References to texts on quantum mechanics are given in the bibliography at the end of this chapter.

1.2 The Evolution of Quantum Theory

During the late nineteenth century evidence began to accumulate that classical newtonian mechanics, which was completely successful on a macroscopic scale, was unsuccessful when applied to problems on an atomic scale.

In 1885 Balmer was able to fit the discrete wavelengths λ of part of the emission spectrum of the hydrogen atom, illustrated in Figure 1.1, to the empirical formula

$$\lambda = \frac{n'^2 G}{n'^2 - 4} \tag{1.1}$$

where G is a constant and $n' = 3,4,5, \ldots$. In this figure the wavenumber† $\tilde{\nu}$ and the wavelength λ are used: the two are related by

$$\tilde{\nu} = \frac{1}{\lambda} \tag{1.2}$$

Using the relationship

$$\nu = \frac{c}{\lambda} \tag{1.3}$$

where ν is the frequency and c the speed of light in a vacuum, equation (1.1) becomes

$$\nu = R_H \left(\frac{1}{2^2} - \frac{1}{n'^2} \right) \tag{1.4}$$

†See Units, Dimensions and Conventions on p. xv.

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