MODERN SPECTROSCOPY

Fourth Edition

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Preface to first edition

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 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 (NMR and ESR), nuclear quadrupole resonance spectroscopy (NQR), 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

Preface to second edition

A new edition of any book presents an opportunity which an author welcomes for several reasons. It is a chance to respond to constructive criticisms of the previous edition which he thinks are valid. New material can be introduced which may be useful to teachers and students in the light of the way the subject, and the teaching of the subject, has developed in the intervening years. Last, and certainly not least, there is an opportunity to correct any errors which had escaped the author's notice.

Fourier transformation techniques in spectroscopy are now quite common—the latest to arrive on the scene is Fourier transform Raman spectroscopy. In Chapter 3 I have expanded considerably the discussion of these techniques and included Fourier transform Raman spectroscopy for the first time.

In teaching students about Fourier transform techniques I find it easier to introduce the subject by using radiofrequency radiation, for which the variations of the signal with time can be readily detected—as happens in an ordinary radio. Fourier transformation of the radiofrequency signal, which the radio itself carries out, is quite easy to visualize without going deeply into the mathematics. The use of a Michelson interferometer in the infrared, visible or ultraviolet regions is necessary because of the inability of a detector to respond to these higher frequencies, but I think the way in which it gets over this problem is rather subtle. In this second edition I have discussed Fourier transformation, relating first to radiofrequency and then to higher frequency radiation.

In the first edition of *Modern Spectroscopy* I tried to go some way towards bridging the gulf that often seems to exist between high resolution spectroscopy and low resolution, often analytical, spectroscopy. In this edition I have gone further by including X-ray fluorescence spectroscopy and inductively coupled plasma atomic emission spectroscopy, both of which are used almost entirely for analytical purposes. I think it is important that the user understand the processes going on in any analytical spectroscopic technique that he or she might be using.

In Chapter 4, on molecular symmetry, I have added two new sections. One of these concerns the relationship between symmetry and chirality, which is of great importance in synthetic organic chemistry. The other relates to the connection between the symmetry of a molecule and whether it has a permanent dipole moment.

In the chapter on vibrational spectroscopy (Chapter 6) I have expanded the discussions of inversion, ring-puckering and torsional vibrations, including some model potential functions. These types of vibration are very important in the determination of molecular structure.

The development of lasers has continued in the past few years and I have included discussions of two more in this edition. These are the alexandrite and titanium–sapphire lasers. Both are solid state and, unusually, tunable over quite wide wavelength ranges. The titanium–sapphire laser is probably the most promising for general use because of its wider range of tunability and the fact that it can be operated in a CW or pulsed mode.

Laser spectroscopy is such a wide subject, with many ingenious experiments using one or two CW or pulsed lasers to study atomic or molecular structure or dynamics, that it is difficult to do justice to it at the level at which *Modern Spectroscopy* is aimed. In this edition I have expanded the section on supersonic jet spectroscopy, which is an extremely important and wide-ranging field.

I would like to thank Professor I. M. Mills for the material he provided for Figure 3.14(b) and Figure 3.16 and Dr P. Hollins for help in the production of Figures 3.7(a), 3.8(a), 3.9(a) and 3.10(a). The spectrum in Figure 9.36 will be published in a paper by Dr J. M. Hollas and Dr P. F. Taday.

J. Michael Hollas

Preface to third edition

One of the more obvious changes from the second edition which *Modern Spectroscopy* has undergone concerns the page size. The consequent new format of the pages is much less crowded and more user friendly.

Much of the additional material is taken up by what I have called 'Worked examples'. These are sample problems, which are mostly calculations, with answers given in some detail. There are seventeen of them scattered throughout the book in positions in the text appropriate to the theory which is required. I believe that these will be very useful in demonstrating to the reader how problems should be tackled. In the calculations, I have paid particular attention to the number of significant figures retained and to the correct use of units. I have stressed the importance of putting in the units in a calculation. In a typical example, for the calculation of the rotational constant B for a diatomic molecule from the equation

$$B = \frac{h}{8\pi^2 c\mu r^2} \quad \text{where} \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

it is an invaluable help in getting the correct answer to check the units with which μ has been calculated and then to put the units of all quantities involved into the equation for B.

Molecules with icosahedral symmetry are not new but the discovery of the newest of them, C_{60} or buckminsterfullerene, has had such a profound effect on chemistry in recent years that I thought it useful to include a discussion of the icosahedral point group to which C_{60} belongs.

Use of the supersonic jet in many branches of spectroscopy continues to increase. One technique which has made a considerable impact in recent years is that of zero kinetic energy photoelectron (ZEKE-PE) spectroscopy. Because of its increasing importance and the fact that it relates closely to ultraviolet photoelectron spectroscopy (UPS), which is described at length in earlier editions, I have included the new technique in Chapter 9.

Charge coupled device (CCD) detectors are being used increasingly in the visible and ultraviolet regions. At present these are very expensive but I have anticipated their increasing importance by including a brief description in Chapter 3.

There are some quite simple symmetry rules for dividing the total number of vibrations of a polyatomic molecule into symmetry classes. The principles behind these, and the rules themselves, have been added to Chapter 4.

I would like to thank Professor B. van der Veken for the improved FTIR spectrum in Figure 6.8.

J. Michael Hollas

Preface to fourth edition

Spectroscopy occupies a very special position in chemistry, physics and in science in general. It is capable of providing accurate answers to some of the most searching questions, particularly those concerning atomic and molecular structure. For small molecules, it can provide accurate values of bond lengths and bond angles. For larger molecules, details of conformation can be obtained. Is a molecule planar? If it is non-planar, what is the energy barrier to planarity? Does a methyl group attached to a benzene ring take up the eclipsed or staggered position? Is a *cis* or *trans* conformation more stable? Spectroscopy provides techniques that are vital in chemical analysis and in the investigation of the composition of planets, comets, stars and the interstellar medium.

At the research level, spectroscopy continues to flourish and is continually developing with occasional quantum leaps. For example, such a leap resulted from the development of lasers. Not all leaps provide suitable material for inclusion in an undergraduate text such as this. However, even in the relatively short period of seven years since the third edition, there have been either new developments or consolidation of rather less recent ones, which are not only of the greatest importance but which can (I hope!) be communicated at this level.

New to the fourth edition are the topics of laser detection and ranging (LIDAR), cavity ring-down spectroscopy, femtosecond lasers and femtosecond spectroscopy, and the use of laser-induced fluorescence excitation for structural investigations of much larger molecules than had been possible previously. This latter technique takes advantage of two experimental quantum leaps: the development of very high resolution lasers in the visible and ultraviolet regions and of the supersonic molecular beam.

Since the first edition in 1987 there has been some loss of clarity in those figures that have been used in subsequent editions. The presentation of figures in this new edition has been improved and small changes, additions and corrections have been made to the text. I am very grateful to Robert Hambrook (John Wiley) and Rachel Catt who have contributed greatly to these improvements. The fundamental constants have been updated. Apart from the speed of light, which is defined exactly, many of these are continually being determined with greater accuracy.

New books on spectroscopy continue to be published while some of the older ones remain classics. The bibliography has been brought up to date to include some of the new publications, or new editions of older ones.

I have not included in the bibliography my own books on spectroscopy. *High Resolution Spectroscopy*, second edition (John Wiley, 1998) follows the general format of *Modern Spectroscopy* but takes the subject to the research level. *Basic Atomic and Molecular*

Spectroscopy (Royal Society of Chemistry, 2002) approaches the subject at a simpler level than *Modern Spectroscopy*, being fairly non-mathematical and including many worked problems. Neither book is included in the bibliography but each is recommended as additional reading, depending on the level required.

I am particularly grateful to Professor Ben van der Veken (University of Antwerp) who has obtained new spectra, with an infrared interferometer, which are shown in Figures 6.8, 6.27, 6.28 and 6.34, and to Dr Andrew Orr-Ewing (University of Bristol), who provided original copies of the cavity ring-down spectra in Figures 9.38 and 9.39.

J. Michael Hollas

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 $=$ $1.602\,176\,462 \times 10^{-19}$ 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 (M), length (L), and time (T) 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 '$m(\text{g})$' is now seen to be incorrect as, algebraically, it could be interpreted only as $m \times \text{g}$ rather than $m \div \text{g}$, which we require.

An issue that 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

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

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

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

is, in words, 'the wavenumber is 20.6 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 20.6 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 make 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 30 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 used for 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 that 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 vibronic 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 for which the conventional number is 32. It is a very neat system compared with, for example, (001) − (100), which is still frequently used for triatomics to indicate a transition from the $v = 1$ level in v_1 in the lower electronic state to the $v = 1$ level in v_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, though, 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.

Fundamental constants

Quantity	Symbol	Value and units†
Speed of light (*in vacuo*)	c	$2.997\ 924\ 58 \times 10^{8}$ m s^{-1} (exact)
Vacuum permeability	μ_0	$4\pi \times 10^{-7}$ H m^{-1} (exact)
Vacuum permittivity	$\varepsilon_0\ (= \mu_0^{-1} c^{-2})$	$8.854\ 187\ 816 \times 10^{-12}$ F m^{-1} (exact)
Charge on proton	e	$1.602\ 176\ 462(63) \times 10^{-19}$ C
Planck constant	h	$6.626\ 068\ 76(52) \times 10^{-34}$ J s
Molar gas constant	R	$8.314\ 472(15)$ J mol^{-1} K^{-1}
Avogadro constant	N_A, L	$6.022\ 141\ 99(47) \times 10^{23}$ mol^{-1}
Boltzmann constant	$k\ (= R N_A^{-1})$	$1.380\ 650\ 3(24) \times 10^{-23}$ J K^{-1}
Atomic mass unit	u $(= 10^{-3}$ kg mol^{-1} $N_A^{-1})$	$1.660\ 538\ 73(13) \times 10^{-27}$ kg
Rest mass of electron	m_e	$9.109\ 381\ 88(72) \times 10^{-31}$ kg
Rest mass of proton	m_p	$1.672\ 621\ 58(13) \times 10^{-27}$ kg
Rydberg constant	R_∞	$1.097\ 373\ 156\ 854\ 8(83) \times 10^{7}$ m^{-1}
Bohr radius	a_0	$5.291\ 772\ 083(19) \times 10^{-11}$ m
Bohr magneton	$\mu_B\ [= e\hbar(2m_e)^{-1}]$	$9.274\ 008\ 99(37) \times 10^{-24}$ J T^{-1}
Nuclear magneton	μ_N	$5.050\ 783\ 17(20) \times 10^{-27}$ J T^{-1}
Electron magnetic moment	μ_e	$-9.284\ 763\ 62(37) \times 10^{-24}$ J T^{-1}
g-Factor for free electron	$g_e\ (= 2\mu_e \mu_B^{-1})$	$2.002\ 319\ 304\ 373\ 7(82)$

† Values taken from Mohr, P. and Taylor, B.N., J. Phys. Chem. Ref. Data, **28**, 1715 (1999), and Rev. Mod. Phys., **72**, 351 (2000). The uncertainties in the final digits are given in the parentheses.

Useful Conversion Factors

Unit	cm^{-1}	MHz	kJ	eV	$\mathrm{kJ\ mol}^{-1}$
1 cm^{-1}	1	29 979.25	$1.986\,45 \times 10^{-26}$	$1.239\,84 \times 10^{-4}$	$1.196\,27 \times 10^{-2}$
1 MHz	$3.335\,64 \times 10^{-5}$	1	$6.626\,08 \times 10^{-31}$	$4.135\,67 \times 10^{-9}$	$3.990\,31 \times 10^{-7}$
1 kJ	$5.034\,11 \times 10^{25}$	$1.509\,19 \times 10^{30}$	1	$6.241\,51 \times 10^{21}$	$6.022\,14 \times 10^{23}$
1 eV	8065.54	$2.417\,99 \times 10^{8}$	$1.602\,18 \times 10^{-22}$	1	96.485
1 $\mathrm{kJ\ mol}^{-1}$	83.5935	$2.506\,07 \times 10^{6}$	$1.660\,54 \times 10^{-24}$	$1.036\,43 \times 10^{-2}$	1