High Resolution Spectroscopy

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Preface

The subject matter which I have tried to cover in this book makes it suitable primarily for postgraduate students and teachers of spectroscopy. At the same time I have attempted to present the material in such a way that it will prove rewarding to an undergraduate student who wishes to read selected sections of the book in order to understand more clearly a part of spectroscopy which may be covered too superficially in an undergraduate text.

In the past ten years or so, development of instrumentation in spectroscopy has caused what was already a vast subject to continue to expand, and at an even greater rate. What makes the increased expansion seem particularly remarkable is that it started at a time when the subject had become somewhat stagnant in the sense that developments tended to be confined to the application of standard experimental techniques to new and interesting molecules.

In this book I have confined myself mostly to what is implied by the title, namely high resolution spectroscopy. In general, this means that the sample is assumed to be in the gas or vapour phase. All the main branches of spectroscopy are covered, the exceptions being electron spin resonance and nuclear magnetic resonance. Photoelectron spectroscopy is included, not because it is basically a high resolution technique, but because the resolution is so much better than in previous attempts to obtain ionization potentials of polyatomic molecules. In addition the subject is so closely related to electronic spectroscopy as to merit inclusion for this reason alone.

It has been my aim to present an overview of microwave, millimetre wave, infrared, visible, ultraviolet, Raman, photoelectron and laser spectroscopy with a bias towards the experimental aspects and to provide the reader with many illustrations of spectra. In the high resolution field such instrumental developments as continuously recording microwave spectrometers, sources for millimetre wave spectroscopy, infrared and visible interferometers, ultraviolet and X-ray photoelectron spectrometers and, particularly, lasers have created revolutionary changes in research and also in teaching. It never has been the case that the most recent advances in research are necessarily too difficult to understand for them to be included in an undergraduate course, and that is probably more true now than ever it was. One example is photoelectron spectroscopy which has been developed almost entirely since 1963 and which seems tailor-made to drive home the validity of the concepts of atomic and molecular orbitals. Another example is provided by lasers which we now read and hear about so much in science

generally that an undergraduate should learn something of their construction and uses.

With such rapid developments in high resolution spectroscopy it has become quite common for advances in restricted parts of the field to be reported in the form of reviews, each written by a different author and published in the mushrooming numbers of review publications. Throughout this book I have referred to many such reviews which have an important part to play in the scientific literature. Complementary to these is a book, such as this one, in which a single author is able to stress the unifying aspects of all the branches of the subject. Such unification is probably more easily appreciated by today's spectroscopists than those of say twenty years ago. In those days many spectroscopists had to build their own instruments which necessitated, for example, a microwave spectroscopist having to be an electronics expert and an infrared or ultraviolet spectroscopist requiring a thorough knowledge of optics. It is not surprising that acquiring this expertise, building instruments and recording spectra in one branch of spectroscopy took so much time that those who were able to make important contributions in more than one branch were exceptional.

In a book covering such a wide range it is not possible to give a comprehensive list of references. In the first six chapters I have relied mainly on the books and reviews referred to in the Bibliographies (at the end of the chapters) for providing references. The material covered in Chapter 7 and, more especially, Chapter 8 is generally much more recently developed so that I have found it necessary to provide more references for these chapters. The list of references is at the end of the book.

I have tried as far as possible to avoid acronyms and abbreviations which abound in the literature of spectroscopy but which may often confuse the reader.

During the writing of this book I have been greatly helped by stimulating discussions with colleagues at Reading University, particularly Professor I. M. Mills, Professor G. W. Series and Dr A. G. Robiette.

I am especially grateful to Dr J. P. Maier, Dr J. W. C. Johns, Dr A. G. Robiette, Dr J. K. G. Watson and Professor D. H. Whiffen, who have each read through a chapter of the book at the manuscript stage and without whose comments, criticisms and corrections there would be more errors and omissions than those which may still be present, and also to Dr T. Ridley, who helped in checking the proofs.

Some of the figures have been made from original spectra and I wish to express my thanks to the following who supplied them:

Figure 4.13   Professor I. M. Mills
Figure 4.15   Dr A. G. Robiette
Figure 4.21   Dr R. K. Heenan and Dr A. G. Robiette
Figure 4.27   Professor I. Ozier
Figure 4.33   Dr R. J. Butcher
Figure 5.10   Professor S. Brodersen
Figure 5.50   Professor I. M. Mills and Dr P. H. Turner
Figure 5.54   Dr A. G. Robiette
Figure 5.55   Professor I. M. Mills and Dr P. H. Turner
Figure 5.57   Professor H. Wieser
Figure 5.58   Professor I. M. Mills and Dr P. H. Turner
Figure 5.59   Professor I. M. Mills and Dr P. H. Turner
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Figure 6.49   Dr R. F. Barrow

Figure 6.104 Dr A. E. Douglas
Figure 6.105 Dr G. Herzberg
Figure 6.107 Professor I. M. Mills
Figure 8.94 Dr T. Ridley

The rest of the figures, other than those which are reproduced directly from journals or books, have been drawn by Mr H. Nichol and I am very appreciative of the way in which he has managed to interpret my intentions.

My thanks are due also to various typists who have been involved with producing the final manuscript but especially to Mrs A. Gillett who did such an excellent job in typing about three-quarters of it.

J. Michael Hollas

Fundamental constants

Quantity	Symbol	Value and units†
Speed of light (*in vacuo*)	c	$2.99792458(1) \times 10^8 \, \mathrm{m \, s^{-1}}$
Vacuum permeability	μ_0	$4\pi \times 10^{-7} \, \mathrm{H \, m^{-1}}$
Vacuum permittivity	$\varepsilon_0 (= \mu_0^{-1} c^{-2})$	$8.854187818(71) \times 10^{-12} \, \mathrm{F \, m^{-1}}$
Charge on proton	e	$1.6021892(46) \times 10^{-19} \, \mathrm{C}$
Planck constant	h	$6.626176(36) \times 10^{-34} \, \mathrm{J \, s}$
Molar gas constant	R	$8.31441(26) \, \mathrm{J \, mol^{-1} \, K^{-1}}$
Avogadro constant	N_A	$6.022045(31) \times 10^{23} \, \mathrm{mol^{-1}}$
Boltzmann constant	$k (= R N_A^{-1})$	$1.380662(44) \times 10^{-23} \, \mathrm{J \, K^{-1}}$
Atomic mass unit	$u (= 10^{-3} \, \mathrm{kg \, mol^{-1}} \, N_A^{-1})$	$1.6605655(86) \times 10^{-27} \, \mathrm{kg}$
Rest mass of electron	m_e	$9.109534(47) \times 10^{-31} \, \mathrm{kg}$
Rest mass of proton	m_p	$1.6726485(86) \times 10^{-27} \, \mathrm{kg}$
Rydberg constant	R_σ	$1.097373177(83) \times 10^7 \, \mathrm{m^{-1}}$
Bohr radius	a_0	$5.2917706(44) \times 10^{-11} \, \mathrm{m}$
Bohr magneton	$\mu_B [= e\hbar(2m_e)^{-1}]$	$9.274078(36) \times 10^{-24} \, \mathrm{J \, T^{-1}}$
Nuclear magneton	μ_N	$5.050824(20) \times 10^{-27} \, \mathrm{J \, T^{-1}}$
Electron magnetic moment	μ_e	$9.284832(36) \times 10^{-24} \, \mathrm{J \, T^{-1}}$
g-factor for free electron	$\frac{1}{2}g_e (= \mu_e \mu_B^{-1})$	$1.0011596567(35)$

† The uncertainties in the final digits quoted are given in parentheses.

Useful conversion factors

Unit	$\mathrm{cm^{-1}}$	MHz	kJ	eV	$\mathrm{kJ \, mol^{-1}}$
$1 \, \mathrm{cm^{-1}}$	1	29979.25	1.98648×10^{-26}	1.23985×10^{-4}	11.9627×10^{-3}
1 MHz	3.33564×10^{-5}	1	6.62620×10^{-31}	4.13571×10^{-9}	3.99033×10^{-7}
1 kJ	5.03403×10^{25}	1.50916×10^{30}	1	6.24144×10^{21}	6.02205×10^{23}
1 eV	8065.49	2.41796×10^8	1.60219×10^{-22}	1	96.485
$1 \, \mathrm{kJ \, mol^{-1}}$	83.5932	2.50606×10^6	1.66056×10^{-24}	1.03643×10^{-2}	1

Contents

1

Quantization of energy

1.1 Historical evolution of quantum theory

During the late nineteenth century much attention was focused on phenomena which defied explanation in terms of the newtonian laws of classical mechanics. One such phenomenon was the emission spectrum of atomic hydrogen which had been observed to consist of discrete wavelengths rather than the continuous range of wavelengths which classical mechanics predicted. Balmer, in 1885, was able to fit the wavelengths λ, observed in the visible region of the spectrum and comprising what we now call the Balmer series, to the empirical formula

$$\lambda = n'^2 G/(n'^2 - 4) \tag{1.1}$$

where G is a constant and n' is an integer which can take only the values 3, 4, 5, ... For electromagnetic radiation, of which visible light is a part, the frequency v is related to the wavelength by

$$c = v\lambda \tag{1.2}$$

where c is the speed of light. Equation (1.1) can be written more usefully, in terms of frequency, in the form

$$v = R_H[(1/2^2) - (1/n'^2)] \tag{1.3}$$

R_H is the Rydberg constant for hydrogen and is named after Rydberg who, in 1890, proposed that expressions of the form of equation (1.3) should be applicable to the spectra of not only hydrogen but of other elements. In 1908, Ritz realized the importance of the fact implied by equation (1.3) that the frequencies in an atomic spectrum can be expressed as the difference between two terms: in this case the terms are $R_H/2^2$ and R_H/n'^2.

Another phenomenon which could not be interpreted classically was the frequency distribution of radiation from a black body. The distribution of the energy over a range of frequencies and also the way in which the distribution changes with temperature is illustrated in *Figure 1.1*. The attempts by Rayleigh and Jeans in 1900 to derive an equation to reproduce the observations were successful at low frequencies but were unable to predict the maximum in the energy distribution and the decrease at high frequencies. On the other hand, in 1894 Wien had been able to predict how the frequency at which there is a maximum in the energy distribution changes with temperature.

Energy

Visible region of spectrum
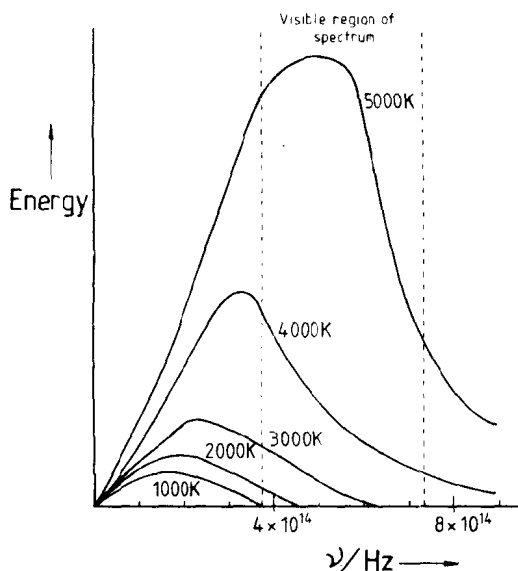
5000K

4000K

2000K 3000K

1000K

4×10^{14} 8×10^{14}

ν / Hz ——►

Figure 1.1   Frequency distribution of black body radiation, and its dependence on temperature

Kinetic energy of photo-electrons
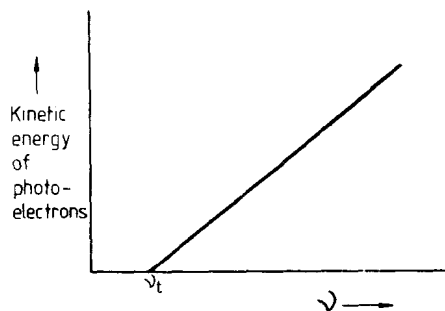
ν_t

ν ——►

Figure 1.2   Dependence of the kinetic energy of photoelectrons on the frequency of incident radiation

The photoelectric effect also defies classical laws. The effect is observed when ultraviolet radiation falls on the surface of a metal. If the frequency of the radiation is continuously increased nothing happens until a frequency ν_t, the threshold frequency, is reached when electrons, so-called photoelectrons, are emitted from the metal surface. As the frequency is increased, further electron emission is instantaneous and the photoelectrons have kinetic energy which is proportional to the frequency. This behaviour is shown in *Figure 1.2*. All metals have their own characteristic threshold frequency. What was expected from classical physics was that the electrons in the metal would require a certain specific amount of energy, known as the work function†, to release them from the surface. If the radiation was of low frequency, i.e. of low energy, then it would take a considerable time, which would be dependent on the quantity of radiation falling on the surface, for the metal to absorb enough energy to release an electron: for radiation of high frequency the time for electron release would be shorter. But the experimental observations are clearly a contradiction of these expectations.

A further difficulty, inexplicable using classical laws, was the temperature dependence of the molar heat capacity, C_v, of a solid at low temperatures. In 1819, Dulong and Petit had derived the expression

$$C_v = 3R \tag{1.4}$$

where R is the ideal gas constant, which requires that C_v is independent of temperature, but this is far from the case at low temperatures, as shown by *Figure 1.3*.

The breakthrough which led to satisfactory explanations of the hydrogen atom spectrum, black body radiation, the photoelectric effect and heat capacities of solids was made by Planck in 1900. His theory of black body radiation requires that the oscillators

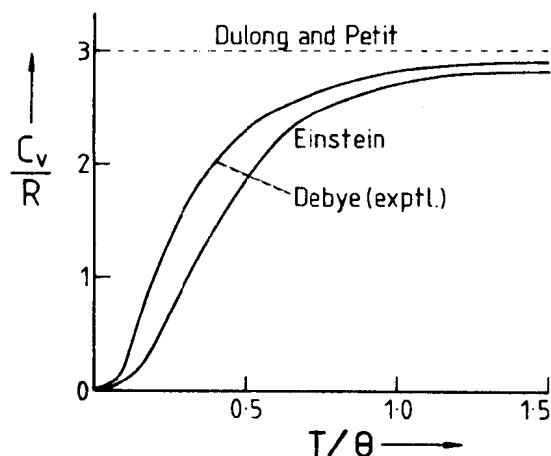† The work function is really a solid-state ionization potential.

Figure 1.3 Temperature dependence of the molar heat capacity, C_v, of a solid at low temperatures. The quantity θ is the Einstein characteristic temperature where $\theta = h\nu/k$

of which a black body is made up and which are responsible for the emission of energy can oscillate only in such a way that the energy E emitted is given by

$$E = nh\nu \qquad (1.5)$$

where n is an integer, ν is the fundamental frequency of the oscillator, and h is a constant which we now know as Planck's constant. The energy is said to be quantized in discrete packets, or quanta, each of magnitude $h\nu$. The expression which Planck obtained for $\rho(\nu)$, the density of radiation of frequency ν for a black body, is

$$\rho(\nu) = 8\pi h\nu^3 \{c^3[\exp(h\nu/kT) - 1]\}^{-1} \qquad (1.6)$$

where c is the speed of light.

The fact that the idea of quantization of energy was not formulated until 1900 was due undoubtedly to its appearing, at first sight, to be at variance with our experience of the macroscopic world. For example, in the case of a simple pendulum swinging at a constant frequency we can give the pendulum *any* energy we choose by starting it swinging with a larger or smaller amplitude. Similarly if we construct a ball and spring model to simulate an oscillator in a black body we can, by choosing the initial impetus which we give to it, choose the energy with which it oscillates.

Part of the answer to this apparent anomaly in the behaviour of microscopic systems, regarded here as those on an atomic or molecular scale, and macroscopic systems is the very small value of Planck's constant: the present accepted value, which dates from 1973, is

$$h = (6.626\,176 \pm 0.000\,036) \times 10^{-34}\,\text{J s} \qquad (1.7)$$

Therefore the magnitude of energy quanta of a simple pendulum oscillating with a period of, say, 1 s is only $6.626\,176 \times 10^{-34}$ J. It is hardly surprising that quantization escaped notice in macroscopic systems!

In 1906 Einstein explained the photoelectric effect in terms of quantization of the energy, in the form of ultraviolet light, falling on the metal surface. Only when the quanta of the radiation have sufficient energy $h\nu$ to overcome the forces binding the electron to the metal, the work function, will a photoelectron be ejected. As the energy and frequency of the radiation increase the excess energy of $h\nu$ over the work function will appear as kinetic energy of the photoelectrons.