Spectroscopy

Molecular, Microwave, Infrared, Far-infrared and Raman Spectroscopy, Force Constants, Group Theory, and Thermodynamic Functions

edited by
B. P. Straughan
and S. Walker

Spectroscopy
VOLUME TWO

EDITED BY

B.P. STRAUGHAN Ph.D., F.R.I.C.
Department of Chemistry,
University of Newcastle upon Tyne,
England

AND

S. WALKER, M.A., D.PHIL., D.Sc.
Chairman, Department of Chemistry,
Lakehead University,
Ontario, Canada

LONDON
CHAPMAN AND HALL
A HALSTED PRESS BOOK
JOHN WILEY & SONS INC., NEW YORK

Preface

It is fifteen years since Walker and Straw wrote the first edition of 'Spectroscopy' and considerable developments have taken place during that time in all fields of this expanding subject. In atomic spectroscopy, for example, where the principles required in a student text have been laid down for many years, there have been advances in optical pumping and double resonance which cannot be neglected at undergraduate level. In addition, nuclear quadrupole resonance (n.q.r.) and far infrared spectroscopy now merit separate chapters while addtional chapters dealing with Mössbauer spectroscopy, photoelectron spectroscopy and group theory are an essential requisite for any modern spectroscopy textbook.

When the idea for a new edition of Spectroscopy was first discussed it quickly became clear that the task of revision would be an impossible one for two authors working alone. Consequently it was decided that the new edition be planned and co-ordinated by two editors who were to invite specialists, each of whom had experience of presenting their subject at an undergraduate level, to contribute a new chapter or to revise extensively an existing chapter. In this manner a proper perspective of each topic has been provided without any sacrifice of the essential character and unity of the first edition.

The expansion of subject matter has necessitated the division of the complete work into three self contained volumes.

Volume 1 includes atomic, n.m.r., n.q.r., e.s.r. and Mössbauer spectroscopy.

Volume 2 contains chapters on molecular symmetry and group theory, microwave, infrared and Raman, far-infrared spectroscopy, force constants, evaluation of thermodynamic functions.

Volume 3 centres on the information which results when a valence electron(s) is excited or removed from the parent molecule. It includes electronic spectroscopy, quantum numbers, dissociation energies, fluorescence and phosphorescence spectroscopy, astrochemistry, photoelectron spectroscopy.

The complete work now provides a single source of reference for all the spectroscopy that a student of chemistry will normally encounter as an undergraduate. Furthermore, the depth of coverage should ensure the books' use on graduate courses and for those starting research work in one of the main branches of spectroscopy.

A continued source of confusion in the spectroscopic literature is the duplication of symbols and the use of the same symbol by different authors to represent different factors. The literature use of both SI and non SI units further complicates the picture. In this book we have tried to use SI units throughout or units such as the electron volt which are recognised for continued use in conjunction with SI units. The symbols and recognised values of physical constants are those published by the Symbols Committee of the Royal Society 1975.

B.P. Straughan
S. Walker

October, 1975

Acknowledgements

Although not involved in the production of this second edition, we would like to express our sincere thanks to Mr. H. Straw whose vital contribution to the first edition of Spectroscopy helped to ensure its widespread success and hence the demand for a new edition. One of us (S.W.) wishes to thank his wife, Kathleen, without whose help at many stages part of this work could not have gone forward.

Contents

1 Introduction to molecular spectra

1.1 ABSORPTION AND EMISSION OF ELECTROMAGNETIC RADIATION

All spectra arise from transitions between energy states, and *molecular spectroscopy* is concerned with the change in internal energy when a molecule absorbs or emits electromagnetic radiation in discrete amounts or quanta.

Molecular energy is divided among several different motions within the molecule, and the measurement of the absorbed or emitted radition gives a value for the energy change involved. A *quantum of energy*, ΔE, is related to the wavelength λ of the radiation by the equation:

$$\Delta E = hc/\lambda$$

where h is Planck's constant and c is the velocity of the electromagnetic radiation in the same medium as the wavelength is measured. In addition, c and λ are related to the frequency, ν, of the electromagnetic radiation by the formula:

$$\lambda \times \nu = c$$

The values of λ and c are slightly dependent on whether the measurements are made in vacuum or in air. The corresponding frequency, however, is in each case given by the same type of ratio which is:

$$\frac{c_{\mathrm{air}}}{\lambda_{\mathrm{air}}} = \frac{c_{\mathrm{vac}}}{\lambda_{\mathrm{vac}}} = \nu$$

If the wavelength measurement is made in air (λ_{air}), it may be corrected to λ_{vac} by the addition to it of $(n - 1)\lambda_{\mathrm{air}}$ where n is the refractive index of air at that particular wavelength.

It is generally more desirable to employ frequency (ν in Hz) rather than wavelength (λ in m) because (energy difference)/h between two molecular energy levels is numerically equal to the frequency of the radiation. This relationship is expressed by the *Bohr frequency rule*:

$$\Delta E/h = \nu\text{Hz} \quad \text{or} \quad \Delta E = E' - E'' = h\nu \text{ joules}$$

and it is the basis for all quantitative spectroscopy. Thus a molecule in an energy state E'' can only be excited into a *higher* energy state E' by the *absorption* of electromagnetic radiation of frequency $\Delta E/h$. Since E' and E'' are essentially precise energies, the absorbed radiation will be essentially monochromatic and all other frequencies will be undiminished in intensity. A spectrum arising from this sort of transition is called an *absorption spectrum.* Alternatively, a molecule may start off in an excited state E' and may undergo a transition to a lower energy state E''. The transition will result in the *emission* of monochromatic radiation of frequency $\Delta E/h$. This process gives rise to an *emission spectrum* which is clearly complementary to an absorption spectrum.

The majority of spectra discussed in these volumes are absorption spectra, i.e. the transitions originate from a ground state. The exceptions include atomic spectra and electronic spectra of diatomic molecules, which are more usually observed in emission, and Raman spectra which arise from a scattering process.

1.2 MOLECULAR ENERGY STATES

It was stated in the previous section that the energy levels of an isolated molecule are *essentially precise.* However, there is some uncertainty associated with the levels, and this uncertainty causes any molecular transition to have a natural line-width. Thus a spectrum does not consist of infinitely sharp lines but the absorptions and emissions appear as broad lines.

Readers will find that some authors in this book write about *line* spectra (which may be sharp, narrow, or broad) whereas others refer to *band* spectra. A distinction can be made if one accepts that a band represents the overall contours which arises when more than one transition has taken place, but the individual energy changes remain unresolved or only partially resolved. For example, if the rotational fine structure associated with a vibrational transition remains unresolved, then the spectrum exhibits a band. If the rotational structure can be fully resolved, then the spectrum consists of a series of rotational lines centred on the position of the vibrational transition. Thus, a line arises from a single transition.

Although this distinction is generally used, the terms tend to become interchangeable in imprecise discussions.

Three factors contribute to the natural line-width of a transition.

1.2.1. Heisenberg's Uncertainty Principle

If a molecule is isolated for a time, Δt seconds, in a particular energy state, then the energy of the state will be uncertain (blurred) to an extent ΔE where:

$$\Delta E \cdot \Delta t \approx \frac{h}{2\pi} \approx 10^{-34}\ \mathrm{Js}$$

h is Planck's constant and the relationship is known as Heisenberg's Uncertainty Principle. If we take into account also the Bohr frequency relationship and write it in terms of an uncertainty in the radiation frequency, $\Delta\nu$, then:

$$\Delta E = h\Delta\nu \approx \frac{h}{2\pi \cdot \Delta t}$$

and hence:

$$\Delta t \cdot \Delta\nu \approx \frac{1}{2\pi}$$

Thus we conclude that the *longer* a molecule remains in a particular energy level, the more precisely the energy will be defined.

For molecular systems it is usual to define the state of zero energy as the *ground state*, and it is conventional to label this state as E''. The latter becomes progressively occupied as the system in thermal equilibrium is cooled towards the absolute zero temperature. The ground state energy of the system will be *sharply* defined because Δt will be large.

In contrast, a molecule may occupy a state of higher energy, i.e. an excited state which is labelled E'. The lifetime of the excited state is usually much less than the lifetime of the ground state, and so the energy is not known precisely. For example, an excited singlet electronic state has a lifetime of 10^{-8} s and hence $\Delta E = 10^{-26}$ J. Assuming that the energy of the ground state is known precisely, a transition from the excited state to the ground state, $E' \rightarrow E''$ will have an uncertainty in the corresponding radiation frequency of:

$$\Delta\nu \approx \frac{1}{2\pi \cdot \Delta t} \approx 10^{8}\ \mathrm{Hz}$$

This uncertainty is small compared with the radiation frequency used to excite transitions between electronic energy levels ($10^{14}-10^{16}$ Hz; see Table 1.1), and so the *natural line-width* is said to be *small*. Compare that situation with an excited *electron spin state* with a lifetime Δt of $\sim 10^{-7}$ s. $\Delta\nu$ is now $\sim 10^{7}$ Hz for a transition to the ground state, and this is of the same order as the usual frequency of radiation used to excite such transitions ($10^{8}-10^{9}$ Hz). This gives rise to a *broad line-width* situation which is a direct consequence of the uncertainty of the energy gap and the region of the electromagnetic spectrum used to excite the particular transition.

1.2.2 Collision broadening

Molecules in the gaseous and liquid phases are never stationary; they continually collide with each other even at temperatures approaching absolute zero. The collisions become more serious as the temperature increases and the buffeting perturbs the energies of the outer electrons as well as the rotational and vibrational energies of the molecules. Thus the collisions cause a blurring of these energy levels, and the corresponding electronic, vibrational, and rotational spectra exhibit *broad* rather than *sharp* lines.

The collisions in liquids are more severe than in gases at ambient temperature, and so the lines in the spectra of gaseous samples are usually sharper than the lines for liquid samples.

The spectra of solid samples are less subject to collision broadening because the random motions of molecules are severely curtailed in the condensed phase. However, the spectra of polycrystalline solids or powders still exhibit broad features caused by unresolved solid-state splitting effects (see Chapter 4, p. 206).

1.2.3 Doppler broadening

The random motions of molecules in the gaseous and liquid states also cause the absorption or emission frequencies to show a Doppler shift. This arises if there is a relative velocity between the instrument detector and the molecules in motion. Since the molecular motions are random, both positive and negative frequency shifts are encountered and a broad line spectrum is observed.

Since the effects of all three types of line broadening are present in a spectrum to some extent, the total line width can be expressed as the sum of all three.

Degeneracy

If two or more states have the same numerical values of energy, they are said to be *degenerate*. Double, triply, four-fold, etc. degenerate states are the names commonly used when 2, 3, 4, etc. energy states have the same numerical value. The degeneracy may be removed (split or lowered are other terms used in this context) by the effect of some external influence such as an electric or magnetic field.

1.3 CLASSIFICATION OF ENERGIES

Since molecules possess a very large number of different types of energy states (e.g. rotational, electronic, etc.), it is essential to use simplifications. The electromagnetic spectrum is usually broken down into various regions, and the regions are associated with a particular type of molecular energy (see Table 1.1). Although the boundaries between the regions are by no means precise, a radiation frequency in a particular region is of the right order of magnitude to bring about a transition between the appropriate molecular energy levels. For example, a frequency of 10^{13} Hz lies in the middle of the *infrared* region and would be associated with *vibrational* energy levels. It is important to remember, however, that Bohr's frequency rule must be obeyed when a *particular* transition is being studied, and that $\Delta E/h$ must be *precisely* equal to ν Hz. The exact frequencies which are required to accomplish the particular energy changes are selected by the molecules from the source of radiation. For absorption and emission processes in a molecule involving electronic, rotation-vibration, and pure rotational changes, it is very rare for only one frequency to be observed. Usually an appreciable number is involved. The set of frequencies at which the absorption occurs enables the molecule to be characterized and identified.

At frequencies above 3×10^{18} Hz (γ-ray region) the energy changes involve the rearrangement of nuclear particles.

In the 3×10^{18}–3×10^{16} Hz region (X-rays) the spectroscopic changes involve the inner electrons of molecules, and the transitions will involve energies of the order of 10^7 J mol^{-1} (~10 eV).

The visible and ultraviolet regions extend from approximately 3×10^{14} to 3×10^{16} Hz, and a transition involves the transfer of a valence electron from one molecular orbital to another. The study of valence electron transitions is called *electronic spectroscopy*, and, because the radiation expressed as a frequency (Hz) leads to very large numbers, it is common to find the frequency expressed as a wavenumber (cm^{-1}) or as a wavelength (nm). Thus 3×10^{15} Hz $\equiv 10^5$ cm^{-1} $\equiv$ 100 nm. The separations between the energy levels of the valence electrons are $\sim 10^5$ J mol^{-1}.

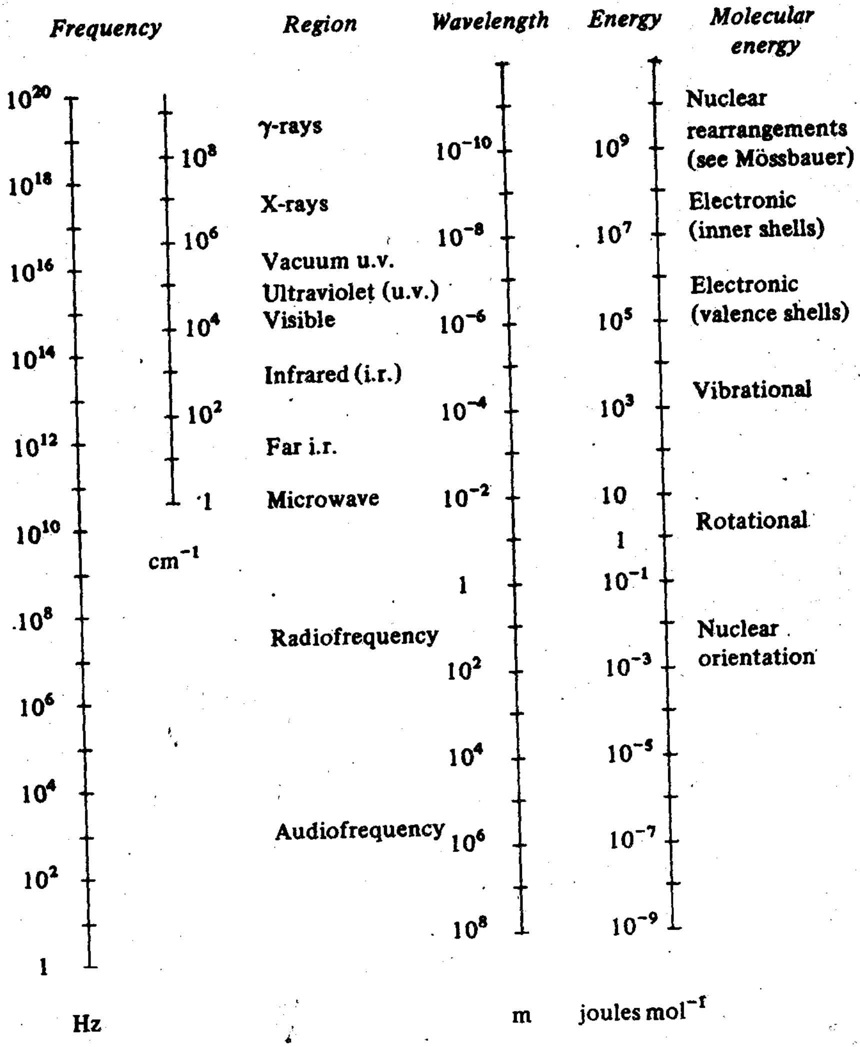
The infrared region is usually quoted as 3×10^{12}–3×10^{14} Hz, and because the energies are mainly associated with the vibrations of molecules, a study of this subject is termed *vibrational spectroscopy*. Again, the region expressed in Hz yields unwieldy numbers, and so the commonest unit is cm^{-1}, i.e. 100–10 000 cm^{-1}. Alternatively, the positions of vibrational bands can be quoted in wavelengths; they will lie in the range 100–1 μm (microns). The separations between vibrational levels are $\sim 10^3$–10^4 J mol^{-1}. The far-infrared region covers the approximate range 6×10^{12}–3×10^{11} Hz (200–10 cm^{-1}) and gives information about the vibrations of molecules containing heavy atoms as well as lattice vibrations.

The microwave region lies in the frequency range 3×10^{11}–10^9 Hz (30 cm to 10 cm^{-1}) and spectroscopy at these frequencies is concerned with transitions between rotational energy levels which are separated by hundreds of joules per mole.

Finally, we come to the radiofrequency region, 3×10^6–10^9 Hz (10 m to 30 cm) where the energy change involved arises from the reversal of spin of a nucleus or electron. The energy is here of the order of only 10^{-3}–10 joules per mole, and the techniques are called *nuclear magnetic resonance* (n.m.r.) and *electron spin resonance* (e.s.r.) *spectroscopy*.

One other spectroscopic technique which is not mentioned in Table 1.1 is

Table 1.1. Regions of the electromagnetic spectrum and associated molecular energies



Useful approximations: $1\ cm^{-1} \approx 10\ J\ mol^{-1}$

$\approx 3 \times 10^{10}$ Hz

$1\ eV \approx 8000\ cm^{-1} \approx 100\ kJ\ mol^{-1}$

Raman spectroscopy. This is a scattering effect which provides information about vibrational and rotational energy levels. The information obtained is often complementary to the results obtained in the infrared and microwave regions but the the Raman scattered light occurs in the visible and ultraviolet regions of the spectrum.

1.4 THE INTENSITY OF SPECTRAL LINES

1.4.1 Transition probability

Whether an energy change can occur at all depends on the ability of a molecule to interact with the electromagnetic radiation. The likelihood of a molecule undergoing a transition from one energy level to another is known as the *transition probability*. The detailed calculation of *absolute transition probabilities* requires a knowledge of the numerical values of the quantum mechanical wavefunctions of the two energy states, and a detailed discussion is beyond the scope of this book. It is much easier, however, to decide whether the transition probability is zero or non-zero, i.e. to deduce the *selection rules* by a qualitative mathematical discussion (see individual chapters).

For example, if the absorption of electromagnetic radiation is to produce a change in vibrational energy, interaction may only take place provided that there is a change in the electric dipole moment of the vibrating unit during the vibration, while for a pure rotational energy change the molecule must possess either a permanent electric or magnetic dipole moment.

It is found in practice that transitions do not take place between all the possible energy levels; there are selection rules which limit the number of transitions. Such rules are occasionally defied, but if a transition occurs which is not permitted by the selection rule, then the intensity of that particular spectral transition is usually very low. The theoretical justification for employing such rules is given by wave mechanics, where in order to solve the equations it is necessary to introduce certain limitations. For example, when the wave-mechanical equation is formulated for the absorption or emission of rotational energy of a diatomic molecule, between a higher rotational energy state characterized by the rotational quantum number J' and a lower one characterized by J'', it is found necessary, in order to obtain an acceptable solution for the equation, that:

$$\Delta J = J' - J'' = \pm 1$$

where $(J' - J'')$ is represented by ΔJ. Thus, permissible pure rotational energy changes are limited by this selection rule to transitions between adjacent levels. Transitions with finite intensity are called *allowed* or *active* transitions. Transitions such as $\Delta J = \pm 2, \pm 3, \ldots$ have *zero intensity* and are not observed in the pure rotational spectrum of a diatomic molecule in either the far-infrared or microwave regions; they are termed *forbidden* or *inactive* transitions.

If the eigenfunctions are known for the two energy states between which transitions are being considered, then it is in theory possible to determine the selection rules, i.e. to decide which transitions are permissible. It should be noted that even if a transition is theoretically permissible, it does not follow that it will necessarily be experimentally detected.

In the analysis of all types of spectra, selection rules are found to be necessary, and examples will be found in individual chapters.

1.4.2 Population of energy states

In addition to the transition probability, the intensity of a transition depends upon the number of molecules which are in the state corresponding to the starting point of the transition. The number of molecules n_i in an upper state i relative to the number of molecules n_j in a lower state j is given by the Boltzmann law of energy distribution. For a system in thermal equilibrium:

$$\frac{n_i}{n_j} = \frac{g_i}{g_j} \mathrm{e}^{-\Delta E/kT}$$

where ΔE is the energy difference between the two states, T is the temperature in K, g_i and g_j are the degeneracies or statistical weights of the two states, and $k = 1.38 \times 10^{-23}\ \mathrm{J\,K^{-1}}$ is the Boltzmann constant. The reader can easily confirm that, if T is room temperature, then the number of molecules in an excited electronic state ($\Delta E \approx 10^6\ \mathrm{J\,mol^{-1}}$) is negligible whereas excited rotational energy levels ($\Delta E \approx 100\ \mathrm{J\,mol^{-1}}$) are well populated up to quite high J values (see p. 82). Thus, in an electronic absorption spectrum at room temperature, only those transitions which arise from the ground electronic state are observed. The rotational spectrum, however, normally contains lines whose transitions originate from excited rotational energy levels.

In conclusion, we have seen that a spectral transition has the important properties of position (i.e. frequency) and intensity. Both of these parameters will be developed further in the chapters dealing with individual techniques because they will usually form the basis of any spectroscopic discussion.

2 Molecular symmetry and group theory

2.1 INTRODUCTION

Molecules are able to possess shape because of the disparity in mass between nuclei and electrons. The nuclei are subject to forces arising largely from their mutual repulsion and an electric field provided by the much more rapidly moving electrons: a field which changes continuously in response to the nuclear configuration. In stable molecules these forces restrain the nuclei to the neighbourhood of an equilibrium configuration, corresponding to a well-defined potential energy minimum. For many sets of atoms several such minima exist. If these correspond to quite different configurations and are separated by high potential barriers they are referred to as isomers, they are chemically separable and are regarded as distinct compounds. On the other hand, relatively low barriers may separate one conformation from another. Such may be the case if one part of a molecule rotates with respect to the remainder, or if a non-planar molecule undergoes inversion. Not all such conformations will be distinct, but even those that are will not easily be separated. Nevertheless such configurations may still usefully be regarded as distinct entities, and throughout this chapter molecules will be considered as having one definite equilibrium shape.†

Because molecules possess shape, identical nuclei occupy equilibrium locations that are geometrically distinct but may usually be related to each other by a set of well-defined movements in space. Identical particles are inherently indistinguishable, and any hypothetical operation which interchanges them (with due regard for the conservation of spin) must leave the molecule unchanged. Such

---

† Readers are referred to Longuet-Higgins [2.9] for a treatment of molecules with several potential minima.

permutation operations include those which carry out movements on the molecule as a whole, bringing it into coincidence with itself. These latter movements are called *symmetry operations*, although this 'active' definition of their nature could be replaced by a 'passive' one in which the transformation is applied not to the molecule itself but to the coordinate system we use to describe it. Thus a forward rotation of a molecule, having the shape of an equilateral triangle, through an angle $+2\pi/3$, is equivalent to a backward rotation of the axes through $-2\pi/3$, as in Fig. 2.1.

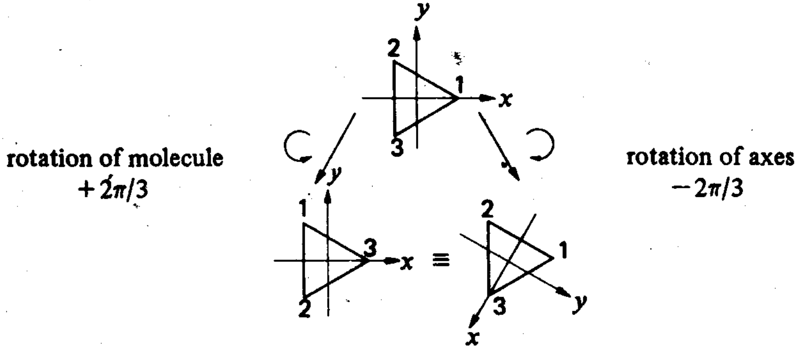


Fig. 2.1

This equivalence emphasizes the fact that a symmetry operation amounts to no more than a renumbering of identical particles and cannot therefore change any observable property of a molecule, such as its energy or the probability of its undergoing a transition from one state to another. We shall find this equivalence useful when applying symmetry operations to molecular systems but in order to give an unambiguous meaning to symmetry operation we shall take the 'active' *definition* because this is somewhat easier to visualize when describing the various kinds of symmetry operation and their relationships.

Although symmetry operations cannot affect observable quantities, they do generally change the molecular wavefunctions. Thus, in the simple case of a non-degenerate wavefunction, if ψ_i is a solution of the Schrödinger equation, $\mathbf{H}\psi_i = E_i\psi_i$, then $a\psi_i$ is also a solution corresponding to the same eigenvalue E_i, where a is any number, real or complex. However, if all solutions are normalized, the modulus of a can only be unity, and if a is real, $a = \pm 1$. Some symmetry operations therefore may leave ψ_i unchanged, but others may change it to $-\psi_i$: its pattern of behaviour with respect to the different symmetry operations characterizes what we shall later refer to as its *symmetry species*. The situation for degenerate wavefunctions is more complicated, but in all cases *the symmetry behaviour can be used to classify and label solutions of the Schrödinger equation.*

Observable quantities, such as those mentioned, are given, according to quantum mechanics, by integrals $\int \psi_n \Omega \psi_m \, d\tau$ involving two wavefunctions ψ_n and ψ_m and an operator Ω. For quantities like energy, which refer to a single