1
Introduction

Molecular physics is at the heart of chemistry and physics. A thorough understanding of chemical and biological processes has been rendered possible only by detailed investigations of the structure and dynamics of the molecules involved. A striking example is the question of chemical bond strength, which is of crucial importance for the course of chemical reactions. Molecular physics traces bond strengths back to the geometrical structure of the molecule's nuclear framework and the spatial distribution of the molecular electron density. The reason for the chemical inertness of the rare gases or the high chemical activity of the alkali metals could only be explained after the structure of the electron shell was understood.

The electron distribution in a molecule can be calculated quantitatively with the aid of quantum theory. Hence, only the application of quantum theory to molecular physics has been able to create a consistent model of molecules and has made theoretical chemistry (quantum chemistry) so successful.

Today's knowledge on the structure of molecules with electrons and nuclei as their building blocks, on the geometric arrangement of nuclei in molecules and on the spatial and energetic properties of the electron shell is based on more than 200 years of research in the field. The origin of this research was characterized by the application of a rational scientific method aiming at quantitative reproducible experimental results. This constitutes the fundamental difference between "modern chemistry" and "alchemy", which contained many mystic elements. The results obtained in these two centuries have not only revolutionized our image of molecules but have also shaped our way of thinking. A similar process can be observed at present, related to the application of physical and chemical methods to biology, where the molecular structures under investigation are particularly complex and the experimental methods employed must therefore be particularly subtle.

It is interesting to take a brief look at the historical development of molecular physics. For more detailed historical accounts we refer to the corresponding literature [1.1–1.4]. It is in many cases highly instructive to read the original research papers which proposed new ideas, models, and concepts for the first time – often in an unprecise form, sometimes still erroneous. This can fill us with more esteem for the

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achievements of previous generations, who had to work with much less perfect equipment than we are used to today, yet obtained results which are often re-discovered even today and are sometimes considered new. For this reason we will often cite the original literature in this book, even though the corresponding results may already be found in textbooks of molecular physics, perhaps even presented with more didactic skill.

1.1
Short Historical Overview

The concept of a *molecule* as a combination of atoms emerged relatively late in scientific literature, at some time during the first half of the 19th century. One reason for this is that a large number of experimental investigations was necessary to replace the historical ideas of the "four elements", water, air, earth, and fire, and the later alchemistic concepts of *elements* such as sulfur, mercury, and salt (Paracelsus, 1493–1541) with an atomistic model of matter. A major breakthrough for this model were the first critically evaluated quantitative experiments investigating the mass changes involved in combustion processes, published in 1772 by Lavoisier (1743–1794), who might be called the first modern chemist.

After Scheele (1724–1786) recognized that air is a mixture of oxygen and nitrogen, Lavoisier created the hypothesis that during combustion, substances form a compound with oxygen. From the results of British physicists from the Cavendish circle, who succeeded in producing water from hydrogen and oxygen, Lavoisier was able to deduce that water could not be an element as had long been thought, but that it had to be a compound. He defined a chemical element to be "the factual limit which can be reached by chemical analysis". The publication of Lavoisier's textbook *Traité elementaire de Chimie* in 1772, which marked a breakthrough for the ideas of modern chemistry, finally surpassed the ideas of alchemy.

Lavoisier's quantitative concept of chemical reactions furnished a number of empirical laws such as Proust's law of constant proportions of 1797, which states that the mass proportions of elements in a chemical compound are constant and independent of the way in which the compound was prepared. The British chemist Dalton (1766–1844) was able to explain this law in 1808 on the basis of his atomic hypothesis, which postulated that all substances consist of atoms, and that upon formation of a compound from two elements one or a few atoms of one element combine with one or a few atoms of the second element (as, e.g., in NaCl, H_2O, CO_2, CH_4, Al_2O_3). Sometimes, different numbers of like atoms can combine to form different molecules. Examples are the nitrogen–oxygen compounds N_2O (dinitrogen oxide, laughing gas), NO (nitrogen monoxide), N_2O_3 (nitrogen trioxide), and NO_2 (nitrogen dioxide), where the atomic ratio N:O is 2:1, 1:1, 2:3, and 1:2, respectively. This established the concept of molecules.

Dalton also recognized that the relative atomic weights constitute a characteristic property of chemical elements. This idea was supported by Avogadro, who proposed, in 1811, the hypothesis that equal volumes of different gases at equal temperature and pressure contain an equal number of elementary particles. From the experimental finding that reaction of *one* unit volume of hydrogen with *one* unit volume of chlorine produces *two* unit volumes of hydrogen chloride, Avogadro deduced correctly that the elementary particles in chlorine and hydrogen gas are not atoms but diatomic molecules, that is, H_2 and Cl_2, and that the reaction is therefore $H_2 + Cl_2 \rightarrow 2HCl$. More detailed accounts on this early stage of molecular science can be found in [1.1–1.4]

Although the atomic hypothesis scored undisputable successes and was accepted as a working hypothesis by most chemists, the existence of atoms as real entities was a matter of discussion among many serious scientists until the end of the 19th century. One reason for that was the fact that there were only indirect clues for the existence of atoms derived from the macroscopic behavior of matter in chemical reactions (for example equilibrium properties) while they were not directly observable.

Until the mid-19th century the size of atoms had not been the subject of scientific investigation. This was changed by the development of the kinetic theory of gases by Clausius (1822–1888), who found that the total volume of all molecules in a gas must be much smaller than the volume of the gas at standard temperature and pressure. He arrived at this conclusion by comparing the densities of gases to that of condensed matter (which is about three orders of magnitude smaller in the former) and from the fact that the molecules in a gas can move essentially free, that is, the duration of collisions is small compared to the time between collisions; otherwise the gas could not be treated as an ideal gas with negligible interaction between collision partners (billiard ball model) [1.5].

The investigation of the specific heats of gases puzzled scientists for a long time, because it showed that molecular gases possessed larger specific heats than atomic gases. After Boltzmann, Maxwell, and Rayleigh could show that the energy of a gas in thermal equilibrium is distributed evenly between all degrees of freedom of the particles, and that the energy is $kT/2$ per degree of freedom and particle, it became clear that molecules had to have more degrees of freedom than atoms, that is, the molecules could not be rigid but had to possess internal degrees of freedom. This was the first hint on the internal dynamics of molecules, an idea which established itself only towards the end of the 19th century.

Spectroscopy contributed significantly to the solution of this puzzle [1.6], in spite of the erroneous interpretation that spectra originated from the vibrations of the atoms or molecules against the "ether", and that the wavelengths indicated the frequencies of these vibrations.

Molecular spectroscopy originated during the first half of the 19th century. For example, in 1834 D. Brewster (1781–1868) observed, after spectral dispersion with the aid of a prism, hundreds of absorption lines, extending over the complete visible spectrum like Fraunhofer lines, when he transmitted sunlight through dense NO_2 gas over a vessel with nitric acid [1.7]. This was astonishing to Brewster, because he did not understand why the yellowish-brown NO_2 gas should feature absorption lines in the blue. He predicted that a complete explanation of this phenomenon would provide work for many generations of researchers, and – as we know today – his prediction turned out to be correct.

The importance of a quantitative interpretation of spectra for the identification of chemical compounds was only recognized after the development of spectral analysis in 1859 by Kirchhoff (1824–1887) and Bunsen (1811–1899) [1.8]. After Rowland had succeeded, in 1887, in producing optical diffraction gratings with sufficient precision [1.9], large grating spectrographs could be built, which allowed higher spectral resolutions and which could resolve individual lines at least for small molecules. They allowed the identification of a number of simple molecules by their characteristic spectra. After 1960, the introduction of narrow-band tunable lasers to molecular spectroscopy opened the way for new techniques with a spectral resolution below the Doppler width of absorption lines (see Ch. 12).

1.2
Molecular Spectra

When an atom or a molecule absorbs or emits a photon of energy $h\nu$ it makes a transition from a state with energy E_1 to another state with energy E_2. Energy conservation requires that

$$h\nu = E_1 - E_2 .$$

The states involved can be discrete, bound states with sharply defined energies; in this case the transition takes place at an equally sharply defined frequency ν. In a spectrum such a transition shows up as a sharp line at the wavelength $\lambda = c/\nu$. Frequently, wavenumbers $\tilde{\nu} = 1/\lambda$ are used instead of wavelengths λ or frequencies $\nu = c/\lambda$. On the other hand, unstable, repulsive states, which can lead to a dissociation of the molecule, or states above the molecule's ionization threshold are usually characterized by a more or less broad-ranged frequency continuum, and transitions into or from such states produce a correspondingly broad absorption/emission spectrum.

For atoms, the possible energy states are essentially determined by different arrangements of the electron cloud (electronic states), and each line in the spectrum thus corresponds to an electronic transition. Molecules, however, have additional internal degrees of freedom, and their states are not only determined by the electron cloud but also by the geometrical arrangement of the nuclei and their movements. This make the spectra more complicated.

First, molecules possess more electronic states than atoms. Second, the nuclei in the molecule can vibrate around their equilibrium positions. Finally, the molecule as

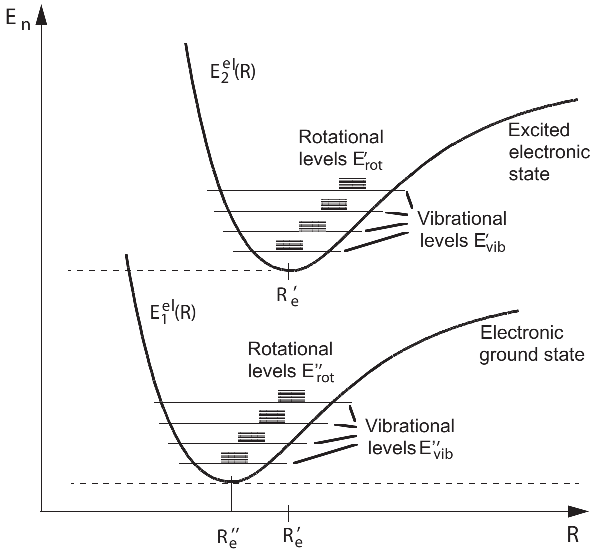

Fig. 1.1 Schematic visualization of the energy levels of a diatomic molecule.

a whole may rotate around axes through its center of mass. Therefore, for each electronic molecular state there exist a large number of vibrational and rotational energy levels (Fig. 1.1).

Molecular spectra can be categorized as follows (Fig. 1.2).

- Transitions between different rotational levels for the same vibrational (and electronic) state lead to pure rotational spectra with wavelengths in the microwave region ($\lambda \approx 1\,\text{mm}$ to $1\,\text{m}$).
- Transitions between rotational levels in different vibrational levels of the same electronic state lead to vibration–rotation spectra in the mid-infrared with wavelengths of $\lambda \approx 2\text{–}20\,\mu\text{m}$ (Fig. 1.3).
- Transitions between two different electronic states have wavelengths from the UV to the near infrared ($\lambda = 0.1\text{–}2\,\mu\text{m}$). Each electronic transition comprises many *vibrational bands* corresponding to transitions between the different vibrational levels of the two electronic states involved. Each of these bands contains many rotational lines with wavelengths λ or frequencies $\nu = c/\lambda$ given by

  $$h\nu = \left(E_2^{\text{el}} + E_2^{\text{vib}} + E_2^{\text{rot}}\right) - \left(E_1^{\text{el}} + E_1^{\text{vib}} + E_1^{\text{rot}}\right),$$

  as required by energy conservation (Fig. 1.2). As an example, Fig. 1.4 shows a section from the band system of the Na_2 molecule with two bands from an electronic transition in the visible spectral range.

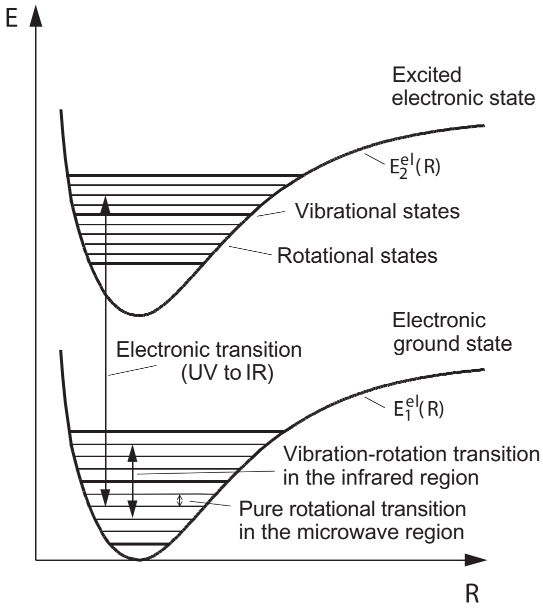

Fig. 1.2 Schematic representation of the possible transitions in diatomic molecules in the different regions of the electromagnetic spectrum.

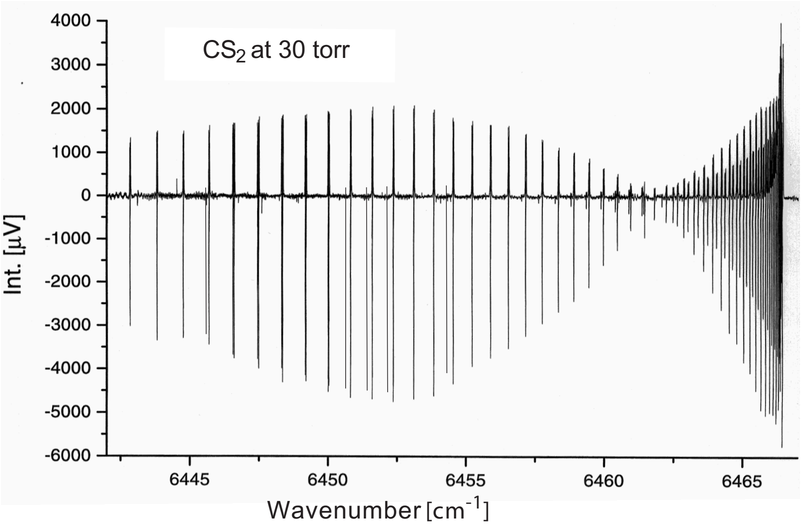

Fig. 1.3 Rotational lines of an overtone vibrational transition of the CS$_2$ molecule with $\Delta v_1 = 2$. (Courtesy H. Wenz, Kaiserslautern)

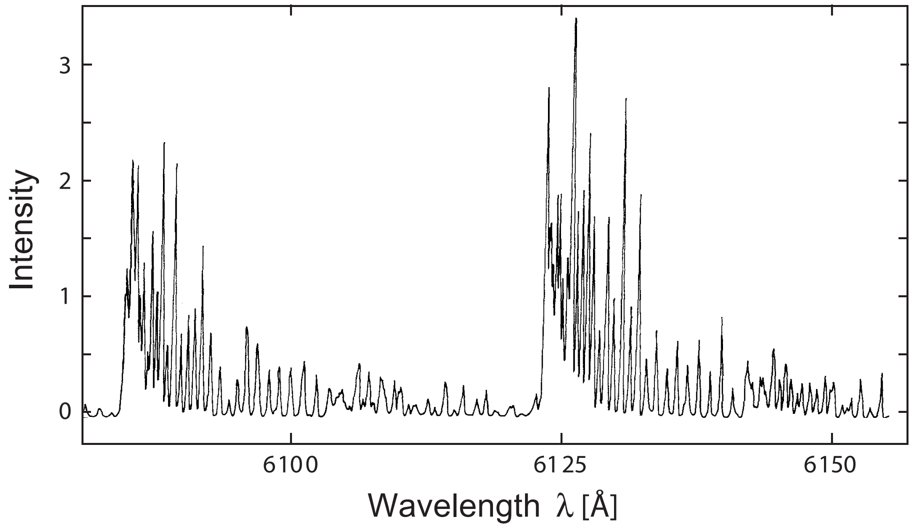

Fig. 1.4 Two vibrational bands from an electronic transition in the Na_2 molecule.

The analysis of a molecular spectrum is usually difficult. It provides a wealth of information, however. The rotational spectra yield the geometrical structure of the molecule, the vibrational spectra give information on the forces between the vibrating atoms in the molecule, and the electronic spectra tell us about the electronic states, their stabilities, and their electron distributions. Linewidths can, under suitable experimental conditions, give information on the lifetimes of excited states or on dissociation energies. The complete analysis of a spectrum of sufficient spectral resolution provides a great deal of information on a molecule. It is therefore worthwhile to put some effort into the complete interpretation of a molecular spectrum.

A deeper understanding of molecular spectra and their connections with molecular structure was achieved only in the 1920s and 1930s with the advent of quantum theory. Soon after the mathematical formulation of the theory by Schrödinger and Heisenberg [1.10, 1.11], a large number of theoreticians applied quantum mechanical calculations to the quantitative explanation of molecular spectra, and even before 1930 numerous publications on problems in molecular physics appeared. In these early publications in molecular physics, it is astonishing to observe how intuition and physical insight enabled great physicists to solve a number of important problems in molecular physics without computers and with very limited experimental equipment (see, for example, [1.12, 1.13]). It is very rewarding to read these early publications, which are therefore frequently cited in the respective sections of this book. Modern textbooks on Molecular Quantum Mechanics are, for example, [1.14, 1.15].

1.3
Recent Developments

It soon became clear that the experimental methods available at the time, that is, “classical” absorption or emission spectroscopy with spectrographs and incoherent light sources, were not able to resolve the individual lines in the spectra of many molecules. At the same time, theoretical efforts to determine the structures of small molecules reliably through *ab initio* calculations, showed some success only for the smallest systems H_2^+ and H_2. Approximations had to be developed and lengthy numerical calculations had to be performed, which were beyond the capacities of the early computers. The focus of theoreticians thus shifted to atomic physics, where many experimental data were available and waiting to be compared to the results of theoretical methods.

During the last 50 years, however, molecular physics has experienced a very active revival. On the side of experimental techniques, the reason is the emergence of many new methods such as microwave spectroscopy, Fourier spectroscopy, photoelectron spectroscopy, the application of synchrotron radiation, and laser spectroscopy. On the theoretical side, high-speed computers with huge memories have enabled quantitative calculations that compete with experimental accuracy in many cases. The mutual stimulation of theoretical prediction and experimental verification (or refutation), or the theoretical explanation of yet unexplained experimental phenomena has produced a great progress in molecular physics. Today it is fair to say that bond energies, molecular structures, and electron distributions of ground-state molecules are essentially understood, at least for small molecules.

The situation is much more difficult for electronically excited molecular states. They are less well investigated than ground states, because only in recent years have experimental techniques been developed that allow the investigation of excited states with the same accuracy and sensitivity as for ground states. Also, they are much more difficult to treat theoretically, which is the reason why there is far less theoretical work on the structures of excited states than of ground states. However, excited states are especially interesting because many chemical reactions occur only after a certain amount of activation energy has been provided, that is, after excited states have been created. For example, this is the case for all photochemical processes, which are initiated by the absorption of light. Also, a detailed understanding of photobiological processes such as the primary visual process or photosynthesis, requires the detailed study of electronically excited states and their dynamics.

Such studies of molecular dynamics are based on the fact that molecules are no geometrically rigid entities but can change their shape. Energy that is “pumped” into a molecule selectively by the absorption of light can alter the electron distribution and can thus bring about a change in the geometrical shape of the molecule (isomerization). The energy can also be distributed evenly between the different degrees of freedom of the molecule, provided they are coupled. This process corresponds to a *heating* of the whole molecule and leads to different results from the selective excitation of specific energy levels.

Interactions between different molecular states, leading to *perturbations* of molecular spectra, are much more common in excited states than in ground states. They can greatly enhance our understanding of the structures of excited states, which can in general not be described by a geometrically well-defined *static* molecular model, because the arrangement of the nuclear framework is constantly changing to adapt to changes in the electron cloud, which can take place at constant total energy (so-called *radiationless transitions*). Especially in large biomolecules, this variable geometric shape is of crucial importance for their biological function [1.16, 1.17].

Recently, the question has been discussed intensively as to whether it is possible to make predictions of the properties of chemical compounds based on the topology of the corresponding molecules. There are indications that for such a topologic analysis the real accurate three-dimensional shape as defined by bond lengths and angles of the molecules is less important than had been thought. It seems more important how many atoms a molecule contains, with how many other atoms each atom is connected, and if the connections form linear chains, rings, crosslinks or combinations of them. If the number of atoms and the number and types of their connections are characterized by index numbers, the topological structure of the molecule can also be characterized by a suitably chosen index number. It is in many cases possible to make correct and useful predictions of the properties of new molecules based on such a topological analysis before an attempt is made to synthesize them [1.18, 1.19].

The development of sensitive detection techniques has enabled the study of unstable molecular radicals, which occur as intermediates in many chemical reactions. They exist usually at very low concentration in the presence of large concentrations of other species, which makes the recording of their spectra a demanding task, especially if nothing is known about the frequencies at which they should occur. Support from theoretical predictions is very important in these cases, and many spectra of such radicals, often also of astrophysical interest, have been recorded successfully primarily on account of a close collaboration between spectroscopists and quantum chemists.

Recently, the study of molecular ions [1.20], of weakly bonded molecules M_n (van der Waals molecules) [1.21] and of larger systems consisting of n equal atoms or molecules (so-called *clusters*) [1.22] has attracted increased attention. Such clusters constitute interesting intermediates between free molecules and liquid drops, and their investigation promises detailed information about the condensation and evaporation processes and the dynamics of larger, loosely bound molecular complexes, which could, under certain conditions, make a transition to an ordered solid (crystal) for large n.

Our detailed knowledge of molecular structure has fostered the overwhelming and exciting progress in biophysics and genetic engineering. These new areas of research will revolutionize our daily life, and may have much more profound consequences than even the development of integrated circuits as a consequence of solid-state research. This alone makes molecular physics a highly topical and important field. In addition, there are many open questions in such boundary areas of molecular physics, which renders the work in molecular physics truly exciting. Before progressing to the forefront of research, however, one must get acquainted with the basic foundations of molecular physics. This book will help in that process by discussing the conceptual and theoretical foundations of molecular physics and by presenting modern experimental methods used in the investigation of molecular structure.

1.4
The Concept of This Book

As the title indicates, this book aims at presenting both the theoretical foundations of molecular physics, the knowledge of which is necessary for a quantitative description of molecules, and modern experimental techniques, which enable the detailed investigation of many molecules. Theoretical and experimental parts are intentionally separated, because this arrangement allows a more consistent presentation especially in the theoretical part, and the common features of experimental methods, such as microwave and laser spectroscopy, can be worked out more clearly.

The theoretical part assumes a basic knowledge in atomic physics and quantum mechanics. The theoretical presentation starts with the introduction of the Born–Oppenheimer approximation, a fundamental concept allowing the separation of nuclear and electronic motion, which is at the heart of each molecular model based on a *nuclear framework* surrounded by an electron cloud. Within the Born–Oppenheimer approximation, the total energy of a molecule can be separated into electronic, vibrational and rotational energies. This is confirmed by spectroscopic results and will be further elucidated in a concise tabulation of the wavelength regions of the different molecular spectra and their classification as rotational, vibrational, and electronic transitions.

The major part of Ch. 2 deals with electronic states of *rigid* molecules, which neither rotate nor vibrate. The basic concepts such as angular momenta and their couplings, symmetries, and molecular orbitals are introduced phenomenologically for electronic states of diatomic molecules. Next, approximation techniques for the calculation of electronic wavefunctions, energies and potentials are presented. The chapter starts with one-electron systems and continues to discuss the problems and techniques for systems with more than one electron. Section 2.8 shows the power of modern quantum-chemical *ab initio* methods for some illustrative examples.

Chapter 3 discusses vibrations and rotations of diatomic molecules. There are in the meanwhile several methods for calculating molecular potentials from *experimentally measured term values* of vibration–rotation levels and for the determination of dissociation energies, which are discussed in detail in the second part of this chapter. The chapter closes with an overview of classical and quantum-mechanical techniques for the treatment of the long-range part of the interaction potential of diatomic molecules for large internuclear separations, which is important especially in scattering experiments.

Chapter 4 deals with the central topic of molecular physics: molecular spectra. All the principal aspects can be discussed and understood for the case of diatomic molecules, where the spectra are easier to analyze. Therefore the chapter is restricted to those, while the spectra of polyatomic molecules are discussed in Ch. 8. Three questions are central:

- Between which states can transitions take place, producing absorption or emission of electromagnetic radiation?
- What is the probability of these transitions?
- What can be learned about molecular structure from the intensities, line profiles, and polarizations of the molecular spectral lines?

In polyatomic molecules, symmetry properties play a crucial role for the simplification and generalization of their representation. Therefore, we discuss molecular symmetry and its representation using group theory in Ch. 5, before we turn to a discussion of vibrations and rotations of polyatomic molecules in Ch. 6, where rotation is presented for the symmetric and asymmetric top. Next, the concept of normal modes of molecular vibration is discussed in detail and is compared with the localized-vibration model, which gives often a better description especially for higher vibrational excitations. The influence of nonlinear coupling on vibrational spectra and the question of chaotic motions is briefly outlined.

The electronic states of polyatomic molecules are discussed with the aim of conveying the most important concepts without going into too much detail. Chapter 7 presents applications of many of the ideas of molecular wavefunctions presented in Ch. 2. The construction of electronic states from molecular orbitals is discussed for some illustrative examples, and the resulting regularities for structure and symmetry of molecules in electronically excited states are emphasized. Chapter 8, dealing with spectra of polyatomic molecules, also uses many of the basics from Ch. 4.

Molecules that can *not* be described within the Born–Oppenheimer approximation are gaining increasing importance in molecular physics. Especially in electronically excited states, molecules often do not possess a fixed geometrical shape but fluctuate spontaneously from one nuclear configuration to another. Such deviations from the Born–Oppenheimer approximation show up in the molecule's spectrum as *perturbations*, where the positions of lines are shifted from their expected values, intensities and linewidths are modified, lines are missing from the spectrum, or completely new and unexpected lines appear. These perturbations make the analysis of spectra more difficult, but they also yield important clues regarding the couplings between different Born–Oppenheimer states. For electronically excited states, they are quite common, and their treatment, described in Ch. 9, is of great importance for a complete and consistent model of excited molecules. As the function of many biologically important molecules depends on such fluctuations of shape, an extension of our static molecular model is essential for applications in biology.

In Ch. 10, we touch briefly on the topic of molecules in external fields. As molecules may possess permanent or induced electric or magnetic moments (dipole, quadrupole, etc.), external electric or magnetic fields can effect shifts or mixing of molecular energy levels. Modern experimental techniques can investigate these effects in detail and have created fascinating applications such as magnetic resonance spectroscopy or magnetic resonance tomography.

A discussion of the interesting topic of van der Waals molecules and molecular clusters, which has been the subject of intensive work in recent years, closes the theoretical part of the book.

Modern experimental techniques, most notably the different methods of spectroscopy, have exerted a strong influence on modern molecular physics. Chapter 12 is therefore devoted to modern methods in molecular spectroscopy.

After an overview of the techniques of microwave spectroscopy for the measurement of rotational spectra, electric and magnetic moments, and hyperfine structures, we present recent methods in infrared spectroscopy such as Fourier spectroscopy, which has largely replaced classical absorption spectroscopy. Infrared laser spectroscopy is also finding new applications continuously as it is in many cases superior to Fourier spectroscopy in terms of spectral resolution and signal-to-noise ratio.

The investigation of radicals and unstable molecules has been made possible by *matrix isolation spectroscopy*, which uses a rare-gas matrix to confine the molecules at temperatures of a few kelvin. This method can thus produce rotation-free spectra of molecules in their lowest vibrational states.

Section 12.3 presents classical techniques of Doppler-limited laser spectroscopy in the visible and ultraviolet and Sect. 12.4 a number of Doppler-free laser-spectroscopic techniques, which allow a selective excitation of specific vibration–rotation levels even in large molecules and thus give new and detailed insight into the structures of excited molecules.

The combination of different spectroscopic techniques has led to the development of double-resonance methods, which offer huge advantages when it comes to the identification of unknown molecular spectra and which allow the application of spectroscopic methods to excited states, which could until now only be applied to ground states. For example, using infrared–microwave double resonance, one can perform microwave spectroscopy in vibrationally excited states, and optical–optical double resonance allows the investigation of high Rydberg states of molecules.

The dynamics of excited states is currently of great interest; it can be monitored using time-resolved spectroscopy. It aims at answering the question, among others, of how and how quickly the excitation energy in a molecule is distributed among the different degrees of freedom, either spontaneously or collision-induced. Such processes can be studied with a time resolution in the femtosecond range ($1\,\text{fs} = 10^{-15}\,\text{s}$). All questions relating to these studies are discussed in Sect. 12.4.12.

Besides laser spectroscopy, there are a large number of spectroscopic techniques, often complementing each other nicely. Of special importance for the study of electronic molecular states is photoelectron spectroscopy, which is therefore discussed in some detail in Sect. 12.5.

The combination of laser spectroscopy and mass spectrometry has proved especially valuable in isotope-specific spectroscopy. The most frequently used types of mass spectrometers are presented in Sect. 12.6.

A notably precise method to measure molecular moments and/or hyperfine structures is radiofrequency spectroscopy, developed by I. Rabi many years ago, which reaches today, employed in combination with laser-spectroscopic techniques, remarkable sensitivity and spectral resolution (Sect. 12.7). Electron spin resonance (ESR) and nuclear magnetic resonance have established themselves as standard tools, and they have reached an enormous importance not only in chemistry and physics but also, in the form of nuclear-resonance tomography, in medicine. They are described in Sections 12.8 and 12.9.

The spectroscopy of radicals using laser-magnetic resonance has helped, among the contributions of microwave spectroscopy, to extend significantly our knowledge of molecules in interstellar space (Sect. 12.4.5).

Although a quantitative description of molecular physics requires a certain mathematical formalism, and although molecular structure cannot be really understood without a firm grounding in quantum mechanics, the author has tried to present all topics as accessible as possible in order to convey physical insight and assist the reader in classifying the multitude of individual phenomena.

There are a large number of good books on molecular physics, some of which are listed in the bibliography. Several aspects and fields are treated in more detail in some of them, while other questions that are important today are missing. In many places throughout this book we cite not only the relevant original literature but also those textbooks which treat the corresponding topic, in the author's opinion, especially clearly. It is my hope that, by its homogeneous coverage of both theoretical and experimental aspects and by its many references to the literature, this book might prove valuable for many chemists and physicists and might thus contribute to a further flourishing of the exciting and important field of molecular physics.