MOLECULAR SPECTRA
and
MOLECULAR STRUCTURE

I. SPECTRA OF DIATOMIC MOLECULES

BY

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With the co-operation, in the first edition, of
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PREFACE

Eleven years ago I published a volume entitled *Molecular Spectra and Molecular Structure I. Diatomic Molecules* which was followed in 1945 by a second volume *Infrared and Raman Spectra of Polyatomic Molecules.* The first volume has been out of print for a number of years but the demand for it seemed to justify a new edition. Although the book has been completely revised and brought up to date, its general plan has remained substantially unchanged. Concerning this plan it seems therefore appropriate to quote from the preface of the first edition:

"I have endeavored to give a presentation which is readable by the beginner in the field and also will be useful to those who do or want to do research work in this field. In order to assist the former, I have frequently made use of small type for those sections that are not necessary for an understanding of the fundamentals. For the benefit of those working in the field, numerous references to original papers have been included.

"A satisfactory presentation of molecular spectra and molecular structure is nowadays not possible without treating thoroughly, apart from the empirical results, the theoretical background also. Therefore I have included as much of the theory of molecular spectra as is possible without going into the more difficult mathematical details. A large number of diagrams, graphical representations of eigenfunctions and potential curves, as well as energy level diagrams, serve to illustrate and to explain the theory. On the other hand, I have added numerous carefully selected spectrograms of bands and band systems (some of which have been taken specially for this purpose) in order to give an accurate idea of the experimental material that forms the basis of the developments.

"While of course most of the material presented is not new, it seems that the actual procedure followed in analyzing a band spectrum has not previously been given as specifically in a book of this kind. The same holds for the applications of band spectra to other parts of physics, to chemistry, and to astrophysics given in the last chapter. I hope that both these features will be found useful."

In the eleven years since the publication of the first edition the subject *Spectra of Diatomic Molecules* has developed vigorously even though not as rapidly as in the preceding two decades. Most of the progress made has been consolidation and slow evolution rather than revolution. Exceptions to this statement are the amazing advances made by applying the new tools of molecular beams and microwaves to diatomic molecular problems.

Naturally I have incorporated these advances of recent years in the present new edition. In addition I have amplified and extended the theoretical sections of the book in response to suggestions of several critics of the first edition. I have added new sections on Radiofrequency (Microwave) Spectra (in Chapter II), Hyperfine Structure (in Chapter V) and Intensities of Electronic Transitions (in Chapter VI) and I have completely rewritten many other sections. In order to improve the presentation and to bring it up to date I have scrutinized every sentence and every illustration. Thus the reader familiar with the old edition will find much revision and modification in detail. Twenty-six new illustrations have been added of which some, like Fig. 57 showing the symmetric top eigenfunctions, have not previously been given in the literature of the subject.

The table of molecular constants of the first edition included only the ground states of all diatomic molecules then known. Following the suggestions of many spectroscopists and in view of the fact that the available tables that include the excited states are now out-dated I decided to undertake the rather arduous task of preparing a comprehensive table of all known states of all known diatomic molecules. This table is presented in the Appendix (Table 39) and now covers 80 pages. I have made every effort to make this table as comprehensive and consistent as possible (see the introduction to it, p. 501). The literature up to September 1949 and in some cases up to February 1950 has been included in the table.

The manuscript of the text matter of the book was completed in August 1948, and only in a few cases was it possible to include later developments in the proofs.

As in the first edition the detailed subject index at the end of the book includes all the more important symbols and quantum numbers used as well as all the molecules treated. Part II of the bibliography of the first edition was taken over and a new Part III added giving all the references to work published since then or to earlier work not used in the first edition.

G. HERZBERG

OTTAWA, ONT.
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CONTENTS

INTRODUCTION

General remarks. In the course of the last three decades, very considerable progress has been made in the investigation and theoretical interpretation of molecular spectra. As a result the study of molecular spectra has become one of the most important, perhaps the most important, means for investigating molecular structure.

From the spectra the various discrete energy levels of a molecule can be derived directly. From these again, we can obtain detailed information about the motion of the electrons (electronic structure) and the vibration and rotation of the nuclei in the molecule. The study of electronic motions has led to a theoretical understanding of chemical valence. From the vibrational frequencies the forces between the atoms in the molecule, as well as the heats of dissociation of molecules, can be calculated with great accuracy. From the rotational frequencies we obtain accurate information about the geometrical arrangement of the nuclei in the molecule—in particular, extremely accurate values of the internuclear distances.

The knowledge of the various properties of the individual molecules so obtained allows us to understand many of the physical and chemical properties of the gases under consideration and, in fact, in many instances allows us to predict these properties—for example, the specific heat and the paramagnetic susceptibility. Also, on the basis of this knowledge, chemical equilibria can be predicted theoretically with great accuracy and chemical elementary processes can be elucidated.

A further important result of the investigation of molecular spectra is that proof has been obtained of the existence of a large number of molecules which were previously unknown in chemistry or were not thought capable of free existence. Among these are CH, OH, C_2, He_2, Na_2, CP, and many others. The structures of these molecules have also been determined.

The investigation of the spectra of diatomic molecules is also of great significance for the physics of atomic nuclei, since certain nuclear properties influence these spectra in a characteristic manner and can therefore be determined from them, and since, furthermore, in some cases rare isotopes may be detected by means of these spectra.

Finally, in recent years, a new field of application of the knowledge of molecular spectra has opened up in astrophysics. Not only can the presence of various molecules on fixed stars, planets, and comets, in the upper atmosphere, and in interstellar space be detected on the basis of their spectra, but also from a more detailed analysis definite conclusions can be drawn concerning the physical conditions in these objects.

This first volume deals with the spectra of *diatomic molecules* and the conclusions that can be drawn from them concerning the structure of these molecules. The spectra of polyatomic molecules will be taken up in the second and third volumes of this series. The former, already published (28),[1] deals with the infrared and Raman spectra; the latter will deal with the electronic spectra of polyatomic molecules. Since a thorough treatment of molecular spectra presumes a certain knowledge of atomic spectra and atomic structure, a short survey of the fundamentals of atomic theory is given in the first chapter of this volume.

The experimental methods for the production and investigation of spectra will not be dealt with here. Reference should be made to Sawyer (4*b*), Harrison, Lord, and Loofbourow (4*c*), Meissner (4*a*), Baly (2), Brode (3), Jenkins and White (6*b*), and Kayser-Konen (1).

The nomenclature of the various quantities concerning the molecule—energy levels, quantum numbers, and so on—was made subject to international regulation in 1930 [Mulliken (515)]. We shall use this *international nomenclature* throughout.

TABLE 1. PHYSICAL CONSTANTS

Velocity of light in vacuum	c	2.99776×10^{10} cm/sec
Planck's constant[1a]	h	$6.623_4 \times 10^{-27}$ erg sec
Electronic charge	e	4.8024×10^{-10} abs. e.s.u.
Electronic mass (rest mass)	m	9.1055×10^{-28} gm
$\frac{1}{16}$ mass of the O^{16} atom	M_1	$1.6597_2 \times 10^{-24}$ gm
Number of atoms in a mol:		
Referred to Aston's atomic weight scale ($O^{16} = 16$)	N_A	6.0251×10^{23}
Referred to the chemical atomic weight scale	N_{ch}	6.0235×10^{23}
Boltzmann's constant	k	1.38033×10^{-16} ergs/degree
Gas constant per mol[2] (chemical)	R	8.31439×10^7 ergs/degree/mol 1.98719 cals/degree/mol
1 thermochemical calorie (defined)[3]	cal	4.18400 abs. joules

Physical constants. The best values of various fundamental physical constants have been the subject of much discussion. We accept here the values recently recommended by DuMond and Cohen (914) which are based on and

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[1] The numbers in parentheses refer to the bibliography, p. 583.

[1a] In an erratum received too late for inclusion in this book, DuMond and Cohen give $6.623_{73} \times 10^{-27}$ for h. The difference is smaller than the probable error.

[2] The gas constant is referred to the standard atmosphere 1013250 dynes/cm^2 as adopted by the International Commission on Weights and Measures [see Rossini (50*b*)] not 1013246 dynes/cm^2 as used by Birge and DuMond.

[3] This *defined calorie* should be distinguished from the calorie of the international steam tables which is used by engineers and defined by 1 I.T. steam calorie = 4.18674 abs. joules. The 15° calorie is given by 1 cal_{15} = 4.1855 abs. joules.

substantially identical with the values derived by Birge (809–811), but we use the defined (thermochemical) calorie recommended by the Bureau of Standards [Mueller and Rossini (1252)] instead of the 15° calorie used by Birge. In Table 1 the values most frequently used in this book are collected. These values differ only very slightly from those used in the first edition of this volume which were taken from an earlier version of Birge's list (107–110) and which are also used in Volume II.

Units and conversion factors. The wave lengths, λ, of the spectral lines in the infrared are measured in μ ($1\mu = 1/1000$ mm) and in the visible and ultraviolet spectral regions in Ångström units (1 Å $= 10^{-7}$ mm $= 10^{-8}$ cm). In theoretical discussions the frequency $\nu' = c/\lambda$ is much more important than the wave length. Instead of it usually the wave number $\nu = \nu'/c = 1/\lambda$ is used which is proportional to the frequency and is measured in cm^{-1} (number of waves per cm). The wave numbers can be given to the same accuracy as the wave lengths and are not limited to the accuracy with which the velocity of light is known. However, in order to have a constant proportionality factor ($1/c_{\text{vac}}$) it is necessary to use the *wave number in vacuo*, which is the reciprocal of the wave length in vacuo. Since the wave lengths of spectral lines above 2000 Å are usually given as measured in air, they have to be converted to vacuum [by adding $(n - 1)\lambda_{\text{air}}$ where n is the index of refraction of air] before the reciprocal is taken. For the region 2000–10,000 Å this calculation can be avoided by using Kayser's Tabelle der Schwingungszahlen (45).[4] According to Babcock (762) the use of these tables can be extended to 5 μ by inverting them and adding a very small correction. For still longer wave lengths $n - 1$ is very nearly constant ($= 2.726 \times 10^{-4}$ at 15° C and 760 mm pressure) so that the vacuum correction is easily made. In infrared work carried out before 1940 the vacuum correction has usually been neglected. This must be kept in mind when molecular constants are calculated from infrared data.

The frequency ν', and the wave number, ν, depend on the energy, E, according to the fundamental Planck relation $E = h\nu' = h\nu c$, where h is Planck's constant. We can therefore take the *wave number as a measure of the energy*, as is very frequently done in spectroscopy. Using the values in Table 1, we find that 1 cm^{-1} corresponds to $1.9855_4 \times 10^{-16}$ erg/molecule. If we wish to refer the energy to 1 mol instead of to a single atom or molecule, we have to multiply by the number of molecules N_{ch} in 1 mol. Therefore, 1 cm^{-1} corresponds to $11.959_9 \times 10^7$ ergs/mol (referred to the chemical atomic-weight scale) or, converting to calories, 2.8584_8 cal/mol.

Another unit used in measuring energy in atomic and molecular physics is the (absolute) *electron-volt* (e.v.). By V e.v. is meant an energy equal to the

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[4] In doing so it must be remembered that Kayser's tables were calculated with values for the index of refraction of air which are now outdated. For very precise calculations the more recent values of Barrell and Sears (770) should be used [see Birge (811)].

kinetic energy of an electron (or singly charged ion) that has been accelerated through a potential difference of V volts. This energy is $eV/299.776$ ergs (the factor $1/299.776$ is introduced in converting to electrostatic units). Substituting the numerical value for e gives 1 e.v. equivalent to $1.60199_6 \times 10^{-12}$ erg/molecule, or 8068.3_2 cm^{-1}, or $23{,}063._2$ cal/mol. These and some other derived conversion factors for the energy units are collected in Table 2.

TABLE 2. CONVERSION FACTORS FOR ENERGY UNITS.

Unit	cm^{-1}	ergs/molecule	cal/mol$_{\text{chem}}$	electron-volts
1 cm^{-1}	1	$1.9855_4 \times 10^{-16}$	2.8584_8	$1.23941_6 \times 10^{-4}$
1 erg/molecule	$5.0364_1 \times 10^{15}$	1	$1.43965_1 \times 10^{16}$	$6.2422_1 \times 10^{11}$
1 cal/mol$_{\text{chem}}$	0.34983_6	6.94612×10^{-17}	1	$4.3359_2 \times 10^{-5}$
1 electron-volt	8068.3_2	$1.60199_6 \times 10^{-12}$	$23063._2$	1