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Vibrational Spectra and Structure of Polyatomic Molecules

多原子分子的结构
及振动光谱

重排本

吴大猷 著

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序　言

物理学是研究物质、能量以及它们之间相互作用的科学。她不仅是化学、生命、材料、信息、能源和环境等相关学科的基础，同时还是许多新兴学科和交叉学科的前沿。在科技发展日新月异和国际竞争日趋激烈的今天，物理学不仅囿于基础科学和技术应用研究的范畴，而且在社会发展与人类进步的历史进程中发挥着越来越关键的作用。

我们欣喜地看到，改革开放三十多年来，随着中国政治、经济、教育、文化等领域各项事业的持续稳定发展，我国物理学取得了跨越式的进步，做出了很多为世界瞩目的研究成果。今日的中国物理正在经历一个历史上少有的黄金时代。

在我国物理学科快速发展的背景下，近年来物理学相关书籍也呈现百花齐放的良好态势，在知识传承、学术交流、人才培养等方面发挥着无可替代的作用。从另一方面看，尽管国内各出版社相继推出了一些质量很高的物理教材和图书，但系统总结物理学各门类知识和发展，深入浅出地介绍其与现代科学技术之间的渊源，并针对不同层次的读者提供有价值的教材和研究参考，仍是我国科学传播与出版界面临的一个极富挑战性的课题。

为有力推动我国物理学研究、加快相关学科的建设与发展，特别是展现近年来中国物理学者的研究水平和成果，北京大学出版社在国家出版基金的支持下推出了"中外物理学精品书系"，试图对以上难题进行大胆的尝试和探索。该书系编委会集结了数十位来自内地和香港顶尖高校及科研院所的知名专家学者。他们都是目前该领域十分活跃的专家，确保了整套丛书的权威性和前瞻性。

这套书系内容丰富，涵盖面广，可读性强，其中既有对我国传统物理学发展的梳理和总结，也有对正在蓬勃发展的物理学前沿的全面展示；既引进和介绍了世界物理学研究的发展动态，也面向国际主流领域传播中国物理的优秀专著。可以说，"中外物理学精品书系"力图完整呈现近现代世界和中国物理

科学发展的全貌,是一部目前国内为数不多的兼具学术价值和阅读乐趣的经典物理丛书。

"中外物理学精品书系"另一个突出特点是,在把西方物理的精华要义"请进来"的同时,也将我国近现代物理的优秀成果"送出去"。物理学科在世界范围内的重要性不言而喻,引进和翻译世界物理的经典著作和前沿动态,可以满足当前国内物理教学和科研工作的迫切需求。另一方面,改革开放几十年来,我国的物理学研究取得了长足发展,一大批具有较高学术价值的著作相继问世。这套丛书首次将一些中国物理学者的优秀论著以英文版的形式直接推向国际相关研究的主流领域,使世界对中国物理学的过去和现状有更多的深入了解,不仅充分展示出中国物理学研究和积累的"硬实力",也向世界主动传播我国科技文化领域不断创新的"软实力",对全面提升中国科学、教育和文化领域的国际形象起到重要的促进作用。

值得一提的是,"中外物理学精品书系"还对中国近现代物理学科的经典著作进行了全面收录。20 世纪以来,中国物理界诞生了很多经典作品,但当时大都分散出版,如今很多代表性的作品已经淹没在浩瀚的图书海洋中,读者们对这些论著也都是"只闻其声,未见其真"。该书系的编者们在这方面下了很大工夫,对中国物理学科不同时期、不同分支的经典著作进行了系统的整理和收录。这项工作具有非常重要的学术意义和社会价值,不仅可以很好地保护和传承我国物理学的经典文献,充分发挥其应有的传世育人的作用,更能使广大物理学人和青年学子切身体会我国物理学研究的发展脉络和优良传统,真正领悟到老一辈科学家严谨求实、追求卓越、博大精深的治学之美。

温家宝总理在 2006 年中国科学技术大会上指出,"加强基础研究是提升国家创新能力、积累智力资本的重要途径,是我国跻身世界科技强国的必要条件"。中国的发展在于创新,而基础研究正是一切创新的根本和源泉。我相信,这套"中外物理学精品书系"的出版,不仅可以使所有热爱和研究物理学的人们从中获取思维的启迪、智力的挑战和阅读的乐趣,也将进一步推动其他相关基础科学更好更快地发展,为我国今后的科技创新和社会进步做出应有的贡献。

"中外物理学精品书系"编委会　主任
中国科学院院士,北京大学教授

王恩哥

2010 年 5 月于燕园

VIBRATIONAL SPECTRA and STRUCTURE of POLYATOMIC MOLECULES

being
An Essay in Commemoration of the Fortieth
Anniversary of the National University of
Peking

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SECOND, REVISED EDITION, 1946
WITH SUPPLEMENT

Dedicated

TO MY WIFE

KUAN-SHIH YUAN WU

PREFACE

During the last ten years or so, considerable amount of information concerning the structure of polyatomic molecules has been obtained through the theoretical studies with the help of the wave mechanics on the one hand, and the experimental investigations of the infrared and the Raman spectra on the other. Lately, there has appeared a number of books and monographs which taken together cover every aspect of the subject. Schaefer and Matossi's Das Ultrarote Spektrum, Kohlrausch's Der Smekal-Raman Effekt and the recent Ergänzungsband, Sponer's Molekülspektren, Stuart's Molekülstruktur, the chapters by Teller and by Mecke in Eucken-Wolf's Hand-und Jahrbuch der chemischen Physik, Bd 9 /II, Plazcek's article in Marx's Handbuch der Radiologie, Bd 6 /II, 2nd edition, and Dennison's article in the Review of Modern Physics, Vol. 3, 1931, deal with either the empirical or the theoretical side of the problems of the vibrational spectra of molecules. Some explanation would indeed be necessary for the present attempt to deal with the same subject that has already been so adequately treated.

Just before the present Sino-Japanese war in 1937, the Physics Department of the National University of Peking was planning to start some work in the field of spectroscopy. A course on molecular spectra was organized. The treatment of the theoretical parts of the subject was largely based on the works of Dennison and Teller. In presenting the experimental data and their interpretations, it was felt that the treatments of the individual molecules in the afore-mentioned works are usually by necessity too brief and in a few cases they need some changes in view of more recent experimental data. Since the war, the University was forced to move, first to Chang-sha, and later here. With the complete lack of laboratory equipments, to go on with the projected work becomes impossible. It is thought, however, that opportunity might be taken of the reduced teaching duty and the suspension of experimental work to survey the field in a more detailed and critical manner. The following pages are the result of incorporating some of the more recent investigations into some former notes.

In view of the existence of the above mentioned and other works, it seems

best to confine this work to the vibrational spectra of polyatomic molecules and the informations obtainable from them. Even then, no attempt is made at comprehensiveness: rather only those still comparatively simple molecules are treated for which there exist sufficient data. The emphasis has been laid more on the individual molecules than on the systematics of the spectra of molecules containing similar structural groups. For the latter, reference should be made to Kohlrauch's Ergänzungsband (which is unfortunately not available to the writer). The studies, in the last few years, of molecular association by means of the spectra have not been reviewed in detail; for while it is easy to understand in a qualitative manner the frequency shifts arising from the formation of hydrogen bonds, both quantitative measurements and a quantitative theory do not seem to be at hand. Also the calculations of thermodynamic functions from spectroscopic data have only been briefly summarized, for except in two or three cases (ethane, benzene) these functions are more of chemical than physical interest. An elementary exposition and summary are given of the theoretical background on which the discussions of the empirical data are based, in the hope that they may serve as an introduction to the subject for those not already familiar with the work in this field. A little knowledge of the wave mechanics is assumed. In the main, these introductory chapters are based on the above-mentioned works, in particular, of Dennison and of Teller, to which frequent references are made.

On account of the lack of adequate library facilities, it has not been found possible, nor indeed useful, to quote all the original papers on the subject. For this the writer may perhaps be pardoned, since the works of Schaefer and Matossi, Kohlrausch, Stuart and Sponer give adequate references to practically all earlier papers. It will be obvious that the discussions of the different molecules in Chap. V are far from being uniform. This is necessary from the nature of the molecules and of the data that are available. More weight has naturally been given the high dispersion infrared investigations of which the Michigan Laboratory has perhaps made the most signal contributions. It will be noted how much more definite informations can be derived from a high dispersion and high resolution study than from a low dispersion work which merely locates the positions of the bands. Let us hope that in the near future, many of the molecules for. which only tentative discussions are given here will be subjected to high dispersion investigations.

The writer is indebted to the many authors from whose works he has drawn

so freely, and in particular to Professor D. M. Dennison from whom he first learned the subject of molecular spectra. To the University, he is grateful for arranging to publish this work on the occasion of its Fortieth Anniversary. Finally, he wishes to express his gratitude to his teacher and friend, Professor Y. T. Yao, Director of the Physics Laboratory, but for whose inspiration this work would not have been attempted.

TA-You Wu

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At present at Kun-ming,
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June, 1939.

CONTENTS

CHAPTER I INTRODUCTION:
METHODS OF STUDYING MOLECULAR STRUCTURE

A molecule may be conceived as a number of atomic nuclei imbedded in the field of a distribution of electrons, or as a number of electrons in the field of the nuclei. Just as in an atom, the electrons in a molecule are capable of existing in different energy states. This is established in a direct manner, besides by the results of the analyses of the spectra of molecules, by experiments on the excitation of molecules by electron impacts-similar to the Franck-Hertz experiment for the atoms. In a given electronic state, there is an equilibrium configuration for the atomic nuclei. Now the questions that first present themselves are the following: What are the geometrical form and the dimensions of a molecule in a given electronic state, and in particular, in the normal state? What is the distribution of the electrons? What is the nature of the binding of the different atoms in the molecule? We shall see that informations concerning these different aspects of the problem of molecular structure can be obtained from a variety of experimental and theoretical studies. We shall mention briefly a few of the more direct and fruitful methods in this chapter and devote the rest of the present volume to the discussion of the methods and results obtained from the study of the vibrational spectra of polyatomic molecules.

§ 1. Non-spectroscopic Methods

A) Permanent Electric Moment Measurements

From measurements of the permanent dipole moment of a molecule, one learns about the distribution of the electric charges in the molecule. Thus a zero moment indicates in general a symmetrical distribution. From the dipole moments of a series of molecules containing a certain chemical bond or a certain radical, it is possible to deduce a value for the dipole moment of the bond or radical, the assumptions being made that there is a definite meaning in ascribing a moment to

a bond or radical, and that in a molecule these bond and group moments add together vectorially without greatly affecting the value of one another. This method is useful in deciding between two or more possible structures for certain molecules. It is subject, however, to the following limitations: On the one hand, the above assumption that the moments of different bonds or groups simply add vectorially in a complex molecule is not always valid on account of the induction effect. On the experimental side, it is not always practicable to measure the dipole moments of molecules in the gaseous state, and measurements in the liquid state and in solutions are subject to a number of disturbing factors for which corrections have to be made, sometimes only with difficulties and in a semiempirical manner.

B) Polarization of Scattered Radiations and Kerr Effect

Information concerning the symmetry properties of the electric charge distribution in a molecule can also be obtained through a study of the polarization characters of the coherent scattered radiations (Rayleigh scattering) from the molecule. The scattering process is determined by the polarizability of the molecule, which is in general an ellipsoid. For a molecule which is spherically or tetrahedrally symmetric, the ellipsoid becomes a sphere and an electric moment can be induced with equal ease in all directions. The scattered radiation will in this case be polarized (that is, the electric intensity of the scattered radiations lies in the same direction as that in the incident radiations). In a molecule in general, however, because of the anisotropy, the induced electric moment will not correspond exactly to the direction of the electric vector of the incident radiations and the scattered radiations will be partially depolarized, the degree of depolarization being determined by the structure of the molecule. Thus measurements of the depolarization of the scattered radiations will throw light on the problem of the symmetry of the molecule.

The appearance of double refraction in a substance when placed in an electric field is also closely related to the polarizability of the molecule. A partial orientation of the molecules as the result of the induced moment in the field brings about a difference in the behavior of the molecules in different directions under the action of the incident radiations. From measurements of the so-called Kerr constant of a molecule, it is possible to derive certain information concerning the

anisotropy of the polarizability tensor of the molecule.

C) X-ray and Electron Diffraction Measurements

When a monochromatio beam of X-ray or electrons of suitable energies is directed through a gas or vapor and the diffracted beam received on a photographic plate perpendicular to the original beam, certain intensity patterns are obtained which are symmetrical about the geometrical center of the beam and are characteristic of the particular molecule under investigation. The theory of Debye enables a correlation to be made between the intensity pattern and the internuclear distances in the molecule. By comparing the observed pattern with the theoretical pattern calculated with various assumed internuclear distances, it is possible to determine these distances. These methods have been extensively used in recent years and have yielded the most direct values for the internuclear distances of molecules. They are, however, subject to the following limitations: As the diffraction of X-rays is mainly determined by the electrons in the molecule, the accuracy of the determination of the internuclear distances depends on the accuracy with which the electron distribution is known, or, since this distribution is usually not known with high accuracy, on how good the approximate distribution is. The diffraction of electrons of 40000-50000 volts energies is, however, mainly a nuclear process and the calculated intensity pattern is mainly determined by the nuclear distances. In this case, only the relatively heavy atoms in a molecule contribute appreciably to the diffracted intensity pattern, and to molecules composed of light atoms such as H and D, this method cannot be applied. In this respect, this method and the method of infrared spectroscopy are complementary.

§ 2. Molecular Spectra

Just as in an atom the electrons in a molecule can exist in different energy states. The energy differences between these states can be expected to be in general of the same order as in the atoms. Hence a transition from one to another of these states, when accompanied by a change in the electric moment of the system, will give rise to the emission or absorption of radiation whose frequency is determined by the relation

$$hv = (E_{el})_m - (E_{el})_n \qquad (1)$$

and lies usually in the visible or the ultraviolet region of the spectrum.

In any electronic state, there must be an equilibrium configuration for the atomic nuclei for the molecule to be stable at all. One may thus consider the molecule as a system of particles in stable equilibrium in a potential field. Such a system can, according to mechanics, execute vibrations about the position of equilibrium. The frequencies of these vibrations are determined by the masses of the atoms and by the potential field. [1] They lie approximately between ca. 3500 cm^{-1} (ca. 3μ) in molecules containing the lightest atom H, and 300 cm^{-1} ($\sim 30\mu$) or even lower in molecules containing such heavy atoms as Br or I. According to the quantum theory, the vibrational energy of a molecule is quantized so that there are discrete states with different energies. If in a transition from a vibrational state v to a higher state v' there is a change in the dipole moment of the system (electrons and nuclei), radiation of frequency given by

$$h\nu_v = (E_{vib})_{v'} - (E_{vib})_v \qquad (2)$$

will be absorbed. From a study of the near infrared spectrum ($1\text{-}30\mu$), informations concerning the vibrational states of the molecules can be obtained.

In addition to the electronic motion and the vibrations of the atoms, a molecule can rotate as a whole. According to the quantum theory, the rotational energy of a molecule is also quantized so that there are discrete states with different energies. The frequency associated with a change of the rotational state

$$h\nu_r = (E_{rot})_{r'} - (E_{rot})_r \qquad (3)$$

is in general of the order 20-200 cm^{-1} depending on the moments of inertia of the molecule. Transitions between the rotational states, if the molecule possesses a permanent electric moment, will give rise to the emission or absorption of radiation in the far infrared spectrum ($50\text{-}500\mu$). This spectrum is called the pure rotational spectrum.

When there is a simultaneous change in the vibrational and the rotational states of a molecule, the frequency of the radiation will be given, in a first approximation, by adding (1) and (2),

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[1] Since the vibrational motions are relatively slow compared with the motions of the electrons on account of the great difference in their masses, the electronic structure will be able to adjust itself during these vibrations. It is with a sort of averaged potential field during these vibrations that we are dealing.