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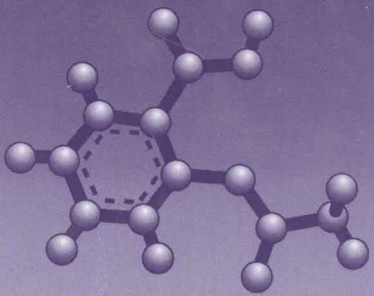

Chemical *Modelling*

APPLICATIONS AND THEORY

Volume 3

senior reporter A. HINCHLIFFE

A Specialist Periodical Report

Chemical Modelling

Applications and Theory

Volume 3

A Review of the Literature Published between
June 2001 and May 2003

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ISBN 0-85404-264-4
ISSN 1472-0965

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Typeset by Charlesworth, Huddersfield, West Yorkshire, UK
Printed by Athenaeum Press Ltd, Gateshead, Tyne and Wear, UK

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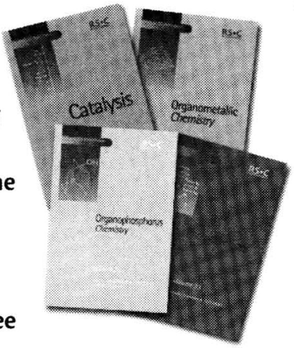

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Preface

Dear Reader,

Welcome to Volume 3 of this SPR. It follows the ground rules that I set out in Volume 1; colleagues reporting on 'new' topics are asked to give the rest of us an easily understandable historical perspective, together with their critical comments on recent developments. Colleagues reporting on continuing topics are simply asked to give a critical review of the literature for the period under consideration.

First of all, I have to thank the regular contributors, whose names and topics you will readily identify from the Contents. It is a pleasure to work with such a nice bunch of people.

I believe that the SPR is fast approaching equilibrium. It is a dynamic equilibrium, with colleagues leaving and joining, so first I should say that Jan van Knop has joined Nenad Trinajstić's team to review enumeration. Second, it is a real pleasure to welcome Karl Travis, who has taken over the liquid state mantle from David Heyes.

Finally I want to mention my old friend Brian Sutcliffe, who writes on the new topic of 'Calculations of the Vibration-Rotation Spectra of Small Molecules'.

The idea of cyclical time has arisen in many different civilizations. The ancient Chinese believed in a cyclical interplay between the opposing cosmic principles of yin and yang, and calculated a cycle of 23 639 years.* They might have had a point for Brian and I both contributed articles to the precursor SPR *Theoretical Chemistry*, which was edited by Richard Dixon and Colin Thomson (although not 23 639 years ago).

It only remains for me to add my usual comment, that there are still a few gaps in the coverage. I'm sure you will have your own ideas what is good and what is bad with this SPR. Rather than grumbling to your colleagues at coffee-time, why not volunteer your expertise? I am always willing to listen to constructive suggestions and can be reached at Alan.Hinchliffe@umist.ac.uk

Better still, I am always willing to consider new topics for inclusion in the SPR. It won't make you a (£ sterling) millionaire, but it gives you the opportunity to promote your subject.

Adam Hinchliffe

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* 'Achilles in the Quantum Universe' by Richard Morris, Souvenir Press, London, 1997.

Contents

Chemical Modelling: Applications and Theory, Volume 3

1

Calculations of the Vibration-Rotation Spectra of Small Molecules

BY B.T. SUTCLIFFE

1 Introduction

It would, I believe, be widely agreed that the modern theory of molecular spectra began with publication by Carl Eckart in 1935 of his paper *Some Studies Concerning Rotating Axes and Polyatomic Molecules.*[1] It would probably also be widely agreed that the apogee of this work occurred in 1968 when James K. G. Watson[2] published *Simplification of the molecular vibration-rotation hamiltonian* which put Eckart's classical mechanical form into a proper quantum mechanical one. This leads to the wave mechanical problem for molecular vibration-rotational motion specified by what we shall call the *Eckart-Watson* Hamiltonian.

This report begins with an account of the theories of molecular spectra that preceded the work of Eckart and the interpretation of spectra that followed his paper during the nineteen forties and fifties. This discussion will involve some consideration of diatomic molecules but they will not subsequently be discussed. So this article is concerned entirely with polyatomic molecules and, in particular those that become linear, only in somewhat excited states. The initial historical discussion, it is hoped, will put the computational work that began in the nineteen seventies into a proper context. During the nineteen eighties and nineties it will be seen that two strands develop in the computational study of molecular spectra. The first is an essentially perturbation theoretic approach, confined almost entirely to the Eckart formulation. The second is a variation theoretic approach which, although sometimes using the Eckart formulation, has found greatest use in formulations using Hamiltonians specifically constructed to describe particular molecules. In referring to such a class of Hamiltonians, they will be called *tailor-made.*

The aim of this this report is to provide an informative context in which relevant examples of computational work on the spectra of small molecules can be presented in a way that, it is hoped, is balanced, fair and comprehensible to the non-expert reader. It is not aimed to provide a comprehensive survey of the literature, since that can nowadays be done in an effective and timely fashion with the aid of facilities on the Internet. Rather it is aimed to

Chemical Modelling: Applications and Theory, Volume 3

provide representative examples of work so that the reader can gain some feeling for what has been done, what is being done and, perhaps, what might be done.

2 History

In December 1926 the US National Research Council published in its Bulletin[3] a Report of the Committee on Radiation in Gases entitled *Molecular Spectra in Gases*. The members of the Committee were Edwin C. Kemble, Raymond T. Birge, Walter F. Colby, F. Wheeler Loomis and Leigh Page. The coordinating editor seems to have been Kemble who, in his *Preface* thanks Professor R. S. Mulliken "whose suggestions and criticisms have been numerous and invaluable".

To put this report in context. Heisenberg's first paper on "the new quantum mechanics" had appeared late in 1925, as had Dirac's first paper, too. Schrödinger's first paper on wave mechanics appeared during February of 1926 and others followed throughout the year. The report was thus written a time of real flux in the underlying theory and its theoretical aspects give testimony to a somewhat uneasy co-existence between the old and new quantum theories, with a strong overlay of classical mechanics, in the theory of molecular spectra.

In his introductory chapter Kemble says that

> the foundation for the present theory of band spectra was laid in 1892 by the older Lord Rayleigh[4] when he pointed out that if an oscillator which at rest emits and absorbs light of frequency ν_0 is caused to rotate with a frequency ν_r about an axis perpendicular to the axis of vibration, then it should emit and absorb in about equal proportions the two frequencies $\nu_0+\nu_r$ and $\nu_0-\nu_r$.

and he goes on to say:

> As early as 1904 Drude[5] from the study of the dispersion of various crystals was led to the conclusion that the infrared absorption spectra and emission bands of most substances, including gases, must be due to the vibrations of electrically charged atoms and molecules rather than to the oscillations of electrons inside the atoms, and in 1912 Niels Bjerrum[6] called attention to the fact that the breadth of the as yet unresolved infrared absorption bands of gases was of the order of magnitude to be expected from the superposition of molecular rotations on molecular vibrations.

These considerations were, at the time being described here, effective only for diatomic molecules and in this case it follows from the Maxwell-Boltzmann law and the classical mechanics of a rigid rotor that a group of molecules in thermal equilibrium at the temperature T the number having rotational frequencies between ν_r and $\nu_r+d\nu_r$ is

$$dn = \frac{4\pi^2 nI}{kT} e^{\frac{-2\pi^2 I\nu_r^2}{kT}} \nu_r d\nu_r$$

where I is the moment of inertia and k is Boltzmann's constant. The quantity dn/dv_r should be proportional to the absorption coefficient for either of the two frequencies $v_0 \pm v_r$ and so the band should be a doublet with a splitting

$$\Delta v = \frac{1}{\pi}\sqrt{\frac{kT}{I}}$$

By 1913, however, experimental techniques had advanced sufficiently for the predicted doublet to be observed and the calculated moments of inertia led to what Kemble justly observed, were "plausible values" for bond lengths. For example the bond length of CO was estimated to be 1.14Åwhile that of HCl was put at 1.34Å.[7] A portion of the near infrared spectrum of of HCl at this level of resolution is given as Figure 30 in Chapter II 2 of ref. 8. By 1914 Bjerrum had developed a theory for CO_2,[9] that treated the vibrations of the system in terms of atoms moving in a potential with a minimum at an isosceles triangle geometry. Among the potentials that he tried were a central field one and a valence field one, this last expressed in terms of a pair of bond oscillators coupled to a bond angle bending oscillator. This was an extremely important step for it introduced a molecular model into molecular spectroscopy. The model idea was that the infrared spectrum of a molecule could be understood if the molecule was looked upon as a vibrating-rotating entity whose vibrations could be interpreted in terms of a collection of point masses moving in a potential with a minimum at a particular geometry with the whole system undergoing free rotation. If a way could be found of attributing particular spectral features to the rotational motion, then it would be possible to establish the moments of inertia of the molecule as a nearly rigid body and from these moments of inertia to determine the geometry of the potential minimum.

Almost simultaneously with these developments however and at about the same time that Bohr's quantum theory came on the scene, further instrumental advances led to the discovery that the diatomic infrared bands were not really continuous but were resolvable into fine structure. A diagram of a portion of the near infrared spectrum of HCl showing this fine structure can be found as Figure 32 in Chapter II 2 of ref. 8. As Kemble remarks:

> It was immediately evident that the existence of this fine structure must be regarded as conclusive evidence for the of the quantization of the rotational motion of the molecules.

In fact the possibility of such quantization had been suggested in 1911 by Nernst and in 1912 by Lorentz but it was Ehrenfest in 1913 who suggested that diatomic quantization should be in multiples of $\frac{1}{2}hv_r$ with

$$v_r = \frac{mh}{4\pi^2 I} \qquad m = 0, 1, 2\ldots$$

and this gave rise to a re-interpretation of the diatomic spectra which, although it yielded a moments of inertia really quite close to those obtained