

Introduction to the theory of molecular vibrations and vibrational spectroscopy

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OXFORD • AT THE CLARENDON PRESS

1972

Oxford University Press, Ely House, London W. 1

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PRINTED IN GREAT BRITAIN
AT THE UNIVERSITY PRESS, OXFORD
BY VIVIAN RIDLER
PRINTER TO THE UNIVERSITY

Preface

As an Oxford Fellow and Tutor for more than a quarter of a century I have had the pleasure of initiating and supervising the experimental researches of a large number of young graduates in the field of molecular vibrational spectroscopy. In consequence I have learned where difficulties with the theory most often arise, and have had considerable experience in helping to deal with them. During sabbatical leave in 1968 as Visiting Professor at the University of Tennessee, I gave a series of about thirty talks on molecular vibrations to a class of doctorate candidates from the faculties of physics and of chemistry. This afforded me the opportunity to assemble and organize the relevant subject matter in note form. The present book is based upon these notes and the discussions to which the talks gave rise.

Nobody undertaking an exposition of this kind could fail to owe an incalculable debt to those two authoritative and extensive works, *Infra-red and Raman Spectra of Polyatomic Molecules* by Herzberg (Van Nostrand, 1945), and *Molecular Vibrations* by Wilson, Decius, and Cross (McGraw-Hill, 1955). I have made frequent use of them ever since their publication. It seemed to me, however, that there was a need for a book on a more modest scale, which would not only expound the essential features of vibrational theory but at the same time would explain and develop the special mathematical ideas and methods involved. The present volume is the result of my attempts to fill this need. It is divided into two related parts, the first of which deals with the classical treatment of the vibrations of molecular models, and the second with the quantum-mechanical theory of vibrational infra-red and Raman spectra. In the course of the exposition the relevant properties and uses of matrices and vectors are explained, and symmetry theory is progressively developed. No attempt is made to deal with a

Preface

broad range of molecular species; on the contrary, all the principal theoretical themes are illustrated by the same few simple examples, which are thus subjected to full and detailed treatment. It is hoped that the book will be found useful, not only by young graduates in physics and chemistry with an interest in vibrational spectroscopic research, but also by experienced workers in related fields and by Honours students.

It is a pleasure to express my gratitude to two Oxford colleagues: to Dr. C. J. Bradley of Jesus College for helpful discussions on symmetry theory, and to Dr. S. Altmann of Brasenose College for kindly reading through the completed work in typescript and sending me his comments. My thanks are also due to the U.S. National Science Foundation for their invitation to spend six months in the United States in 1968 as a Senior Foreign Scientist Fellow, and to the staff of the Chemistry Department of the University of Tennessee at Knoxville (and in particular to Professor W. H. Fletcher) who made me very welcome and gave me facilities for the compilation of the notes which formed the basis for this book. The main work of writing it has been done during the tenure of an Emeritus Fellowship, for which I am much indebted to the Leverhulme Foundation.

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Jesus College, Oxford
1971

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Part I

The treatment of molecular vibrations by classical mechanics

1 A simple example to illustrate the application of classical mechanics

1.1. Reasons for undertaking a classical treatment

THE vibrations of molecules are subject to quantum mechanics. It may well be asked, therefore, why we should undertake a lengthy discussion in terms of classical mechanics. Broadly speaking, the reasons are rooted in the close relationship between the classical and the quantum theories of molecular vibrations, in consequence of which an analysis on the basis of the former will give insight and information which will be very valuable with respect to the latter.

More particularly, our classical treatment will be based upon the assumption (in practice a very good one) that the vibrations are simple-harmonic. In this special case the advantages for later quantum-mechanical treatment are very considerable. We shall be led to introduce special kinds of coordinates in terms of which the classical vibrational problem assumes very simple forms; and when we come to the treatment on the basis of the Schrödinger wave-equation we shall find that the adoption of these same coordinates will effect a corresponding simplification. Moreover, the symmetry properties of the classical coordinates will have very important parallels in the symmetry properties of the wave-mechanical eigenfunctions, upon which the spectroscopic selection rules depend.

The simple-harmonic approximation leads to one especially noteworthy result concerning the actual values of the vibrational frequencies in any particular case. As observed in spectroscopy, a fundamental is the frequency of the radiation absorbed or emitted in consequence of a transition between quantized energy levels. We will designate it by ν_{qu} . On the other hand, the frequency-value calculated by classical theory on the basis

of a suitable model is a mechanical frequency. We will designate it by ν_{cl} . It transpires that $\nu_{\text{qu}} = \nu_{\text{cl}}$. This remarkable and conveniently uncomplicated result is peculiar to vibrations which are simple-harmonic.

1.2. The simple mechanical system to be studied

The remainder of this chapter will be devoted almost entirely to considering a simple mechanical system, without questioning whether such a system could serve usefully as a model of a molecule. The object of this exercise is to illustrate some features

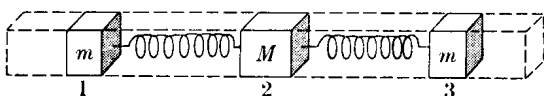


FIG. 1.1. A simple mechanical system to illustrate the application of classical mechanics.

of classical mechanics and, in particular, to familiarize the reader with some of the types of coordinates used. Suitable for our purposes is a system consisting of three masses joined in a straight line by two identical springs of negligible mass. We shall confine our attention to motions along the line of centres. In order to ensure the exclusion of motions in other directions, and also to exclude rotations of the individual masses, we may suppose each to consist of a uniform block of the same square cross-section, able to move in a piston-like manner inside a closely fitting and perfectly frictionless horizontal tube (see Fig. 1.1). For convenience the masses are numbered as shown. The masses 1 and 3 are equal, both having the value m . The central mass 2 has the different value M . When all three are at rest and at equilibrium, the configuration will obviously be such that the centres of masses 1 and 3 will be equidistant from the centre of mass 2.

1.3. Mechanical treatment in terms of simple displacement coordinates

We shall not be concerned with the actual positions of the mass-centres in their equilibrium configuration, but rather with