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This book introduces the reader to the theory and practice of infrared and Raman spectroscopy as applied to the study of the physical and chemical characteristics of synthetic organic polymers. Its purpose is to provide a firm foundation in the subject and a starting point for the study of more-advanced literature. To this end, the book concentrates on the fundamental principles, including many now classic studies in the subject. No previous knowledge either of polymers or of vibrational spectroscopy is assumed.

The book will be of value to anyone beginning research on the vibrational spectroscopy of polymers, from either a physics or a chemistry background, and in particular to research students. Parts of it will be suitable for use in undergraduate courses in physics, chemistry or materials science.

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## The vibrational spectroscopy of polymers

**Cambridge Solid State Science Series**

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## Preface

The aim of this book is to present a coherent introductory account of the theory of vibrational spectroscopy and of its application to the study of synthetic organic polymers. The level of presentation is intended to be suitable for the research student who has previously obtained a degree in either physics or chemistry and who is embarking on research in this area. Such a student would, we hope, read the book in its entirety and then be equipped with sufficient background knowledge and understanding to tackle the specialised literature of the subject with some confidence. We hope that in addition the book will fulfil a similar function for any research worker new to the subject and that parts of it may also be found useful by undergraduate students studying either vibrational spectroscopy or polymer science. To make the book accessible to those new to the study of polymers we have given a brief introduction to the subject in chapter 1. This chapter also contains a brief description of experimental methods in vibrational spectroscopy which is intended to give the reader the minimum amount of information required to follow the rest of the book and to feel that his feet are firmly on the ground. Although we regard the book primarily as one to be read rather than simply referred to, we have provided detailed indexes, since the nature of the subject is such that the spectroscopist needs to master a large number of ideas and facts and easy reference to these is vital if that mastery is to be quickly obtained.

Infrared spectroscopy has been used to characterise synthetic polymers for the whole of the period over which the majority of them have been known, and it is still the more popular of the two vibrational spectroscopic techniques discussed in this book. Raman spectroscopy was very difficult to apply to any material before the advent of the laser in 1960, but since that time the ease of use of the laser as a source has stimulated the development of better Raman spectrophotometers and Raman spectroscopy may now be undertaken quite as routinely as infrared. Its lesser popularity springs largely from its greater expense, but we feel that there is also an element of suspicion in the minds of some that despite the extra expense Raman spectroscopy does not offer any more than infrared for many investigations, and that in any case it is more difficult to understand. In fact, the two techniques are complementary in a variety of ways and there can be no excuse for

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neglecting either unless it be the one of expense. In this book the two methods are treated completely on a par and while we admit that Raman spectroscopy is slightly more difficult to understand than infrared we hope to dispel any fears on this ground.

One of the problems of all spectroscopic techniques is that they involve large amounts of specialised notation and usually attract a corresponding amount of jargon. It is one of the aims of this book to present both of these aspects of Raman and infrared spectroscopy, particularly as applied to polymers, in as simple a way as possible and to give many examples of their use. In order to leave room for a large amount of illustrative material, the theoretical sections do not go into more depth than is necessary for a beginner's understanding. For fuller details the reader is referred to the books listed in the Further Reading sections at the ends of chapters 2, 3 and 4. One piece of jargon that we have tried to avoid entirely is the use of the word 'band' to describe the broadened spectral lines that are observed in the infrared and Raman spectra of polymers. To us that word implies a set of discrete lines very close together and is best avoided since that is not what is implied by its use in the literature of the vibrational spectroscopy of polymers. We have preferred to use words such as 'peak' or 'absorption' and we hope that this idiosyncrasy on our part will not be found confusing.

We owe a great debt to many books, reviews and papers on vibrational spectroscopy in general and on the vibrational spectroscopy of polymers in particular. The books and reviews that we have found most useful are listed in the Further Reading sections at the ends of the chapters. We did feel, however, that in a textbook of this nature the pages should not be peppered with references to individual papers. Our aim has been primarily to illustrate the basic principles of the subject by means of examples where the interpretation of the spectra is now generally accepted as well established, at least in outline. Such acceptance is usually the outcome of the work of a large number of people. In those places where we have relied extensively on the work of particular authors their names will usually occur in the text, in acknowledgments for the use of tables or diagrams or in the list of references for chapters 5 and 6 given at the end of the book. This list is not meant to be comprehensive but to include references to classic papers and to papers that will lead the reader to the literature of a particular topic. We thank all authors whose work we have made use of in preparing the book and especially those who have given us permission to reproduce or adapt their material. We hope that all will forgive us for any inadvertent misinterpretation or oversimplification of their work.

We are very grateful to a number of people who have read drafts of

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various parts of the book, which has benefitted enormously from their comments. In particular, we should like to thank Professor N. Sheppard for reading and commenting in great detail on drafts of chapters 1 to 4: without these comments a large number of errors and obscurities would not have been avoided. Others who read various sections and made valuable suggestions were Professors J. S. Dugdale and G. J. Morgan, Drs G. C. East, L. J. Fina, P. Gans, J. B. Gill, S. J. Spells, A. P. Unwin and J. M. Woodhouse. Professor A. C. T. North rewrote our original version of subsection 6.6.4 and the present version is substantially his. Our greatest debt is to Professor I. M. Ward, both for the original suggestion to write the book and for reading at least two complete drafts. The present structure of the book and the content of a number of sections, particularly in chapters 5 and 6, were influenced greatly by his suggestions. To all these people who contributed to making the book better than it would otherwise have been we offer our thanks, while accepting that, in spite of their efforts, errors and obscurities will remain. We accept full responsibility for these and would be pleased to be informed about them.

Our thanks are due to Dr S. Parker of BP Research Centre, Sunbury, for providing the original spectra for figures 5.1, 5.3, 5.9, 5.14, 5.15, 5.17, 5.18, 5.19 and to Dr P. Spiby for providing the spectrum for figure 4.5. We also thank Mrs M. Edmundson and Mrs G. Garbett for typing parts of the early drafts and the Cambridge University Press for their patience during the long preparation time of this book.

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