

**The Infrared Spectra of  
Complex Molecules**

VOLUME TWO

**Advances in Infrared  
Group Frequencies**

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**Advances in Infrared  
Group Frequencies**

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## Preface to the Second Edition

I have always regarded this book as being the completion of my earlier book, *The Infrared Spectra of Complex Molecules*. The latter sets out all the existing experimental facts on group frequencies in the infrared, but does not attempt to explain them. This present book is primarily concerned to explain why group frequencies move about in the way that they do following changes in substitution. I am therefore very glad that the publishers have decided that the two books should be regarded as Volumes 1 and 2 of a unified work on infrared group frequencies. Both aspects seem to me to be of equal importance. One cannot interpret an infrared spectrum without a good knowledge of the experimental facts, but too rigid an interpretation without any understanding of how these facts originate can lead to gross errors.

Time deals more severely with theories and with chemical mechanisms than it does with the results of experiment, so that this book after ten years has needed very extensive revision. I have rewritten about a third of the text, deleted about an equal amount, and have included about 450 new references from amongst the several thousand that it has been necessary to consult.

Some group frequencies, especially the XH stretching vibrations, are so free from coupling that they do afford a true measure of the bond strengths. A study of the factors which cause these frequencies to change is therefore a study of the mechanisms of chemistry itself. This is an area for which infrared has unique possibilities which have not as yet been fully exploited. A good example is the sizeable variations in the strengths of CH bonds in  $\text{CH}_3$  and  $\text{CH}_2$  groups which have been demonstrated by partial deuteration work. Hydrogen atoms which were previously thought to be equivalent have been shown to be not so, and bond energy differences in the CH bonds of methyl groups have been found to be as large as 13 k cal, in special cases. Two different mechanisms whereby such changes can occur have been shown to exist, mainly through a study of infrared group frequencies, and the results must influence current thinking on chemical mechanisms generally. Studies of this kind have also opened up new possibilities such as the estimation of bond lengths, bond angles, kinetic data and much else. There is scope for much more work in this field, and anyone who ventures into it will find that nearly all the experimental data he needs already exists, so that research of this kind is less tedious than would otherwise be the case, and it can be very rewarding, as I hope this book will show.

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