

The Infra-red Spectra of Complex Molecules

L. J. BELLAMY

B.SC., PH.D.

Principal Scientific Officer, Ministry of Supply

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Chemical Inspectorate, Ministry of Supply

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CHAPTER I

Introduction

INFRA-RED spectroscopy is being employed to an ever-increasing extent in commerce and in organic chemistry for the recognition and the quantitative analysis of structural units in unknown compounds. Almost all the spectrometers employed in industry are used for this purpose, although, in the hands of theoretical physicists, the spectra can also be used to obtain fundamental data on the mechanics of simple molecules. The latter studies are extremely useful to the analyst, in that the particular motions associated with the various characteristic frequencies are determined, so that it is possible to assess to some extent the likelihood of frequency shifts occurring with changes in the local environment of the group. Nevertheless, these studies are necessarily restricted to simple molecules in which the frequencies associated with various structural units are often out of line with those found for more complex materials.

In the interpretation of spectra, therefore, the analyst must rely upon the empirical data which have been accumulated relating infra-red absorption bands with structural units. This involves a very complete knowledge of all the widely scattered work on this subject, and this is not easy to obtain. A number of correlation charts summarising this information have been published from time to time and, properly used, these are of great value. However, as their authors point out, the correlations are of unequal value and, in some cases, are based on the study of limited groups of compounds, so that their incautious use can lead to wholly misleading results. Furthermore, if the frequency ranges given for a specific grouping, such as the carbonyl vibration, were to be extended to cover all the known cases in which interference or interaction effects occur, the final range would be too wide to be of any value; whereas, in fact, the particular point at which a carbonyl absorption appears within this range will often throw a good deal of light on the nature of the adjoining structure.

The present work is, therefore, an attempt to present a critical review of the data on which infra-red spectral correlations are based, indicating the classes of compounds which have been studied in each case and the known factors which can influence the frequencies or intensities of the characteristic bands. In doing so, especial attention has been paid to publications dealing with the groups of compounds containing common structural units and, although a considerable

number of fundamental studies on single molecules have been covered, no attempt has been made to provide a complete bibliography of these, as the absorption of structural units of very simple compounds are often not typical of those found in larger molecules. For ease of reference the chemical names given in the original publications have been retained throughout, although this has involved occasional departures from the accepted British nomenclature. Wherever it has seemed necessary or practicable, the published data has been supplemented by reference to our own library of some two thousand infra-red spectra.

Many of the correlations discussed, particularly those in the high-frequency region, are capable of giving structural information of great value and precision, and the position and intensities of the absorption bands can be used to confirm the presence of a particular group and to obtain information as to its environment. Others, particularly in the region of skeletal vibrations, are subject to considerable frequency alterations with structural change. These can only be employed with caution and cannot safely be applied to structures widely different from those on which the correlations are based. Nevertheless, even these can be of value in indicating possible structures, whilst the absence of any bands in the appropriate region is usually a good indication of the absence of the particular grouping from the molecule. In any case, in work of this type, the spectroscopist is expected to indicate not only the presence of groupings of which he can be reasonably certain, but also to discuss the various structures which may be present but which cannot be identified with certainty. It is in assisting him to determine the proper weight which can be given to any particular identification that it is hoped this book will prove to be of value.

The subject-matter of this book has been strictly confined to the empirical interpretation of infra-red spectra, as this is the topic on which no adequate text has appeared. No attempt has been made to cover the many related aspects of practical spectroscopy, such as sample preparation, cell construction, quantitative analysis, instrumentation, etc. These topics have all been adequately discussed in a number of existing texts and in others which will be available shortly. Furthermore, very few workers in this field are so fortunate as to possess more than one type of instrument, and they rapidly learn by experience far more about its individual characteristics and peculiarities than can be covered in any general review of the subject.

In any book of this kind which deals with a mass of isolated empirical observations about a variety of different structural units, a purely arbitrary arrangement of subject-matter must be employed, and I have followed the general lines of the well-known correlation charts which have appeared in the literature from time to time.¹⁻³

The various types of linkage are roughly classified into four main classes:—

I. Carbon-carbon and carbon-hydrogen links. II. Carbon-oxygen and oxygen-hydrogen links. III. Carbon-nitrogen and nitrogen-hydrogen links. IV. Linkages involving other elements, or which are related to inorganic structures. This arrangement has not however been followed too rigidly. The discussion on amides, for example, cannot be divided between parts II and III; and it has been included at the head of part III, where it follows directly upon the discussion of carbonyl frequencies in part II. Similarly, the chapter on nitro-compounds and related structures heads part IV, where it follows the discussion of carbon-nitrogen linkages.

As regards the choice of units, I have employed wave-numbers throughout. In choosing to give frequencies rather than wavelengths I have been influenced partly by the recent recommendations of the Royal Society Committee, and partly by my own view that the wave-number scale is the only really satisfactory one for correlation work. The use of this scale makes it much easier to identify overtone and combination bands, and it is especially valuable in enabling direct comparisons to be made with Raman spectra. Probably the most powerful argument which can be advanced for the wave-length scale is the fact that it is easier to construct an instrument which is linear on this basis. For the benefit of those who use such instruments a table of reciprocals is included at the end of the book.

At the beginning of each chapter a brief outline is given of the correlations to be discussed, together with a table giving the various frequency ranges, whilst at the end of this chapter a series of charts is given in which the correlations are summarised in the usual line drawing form. The first is intended to give the reader an outline of the particular correlations which exist before discussing any one of them in detail, whilst the second is designed to enable him to see readily any other structural units which might be expected to absorb in any specific region and which might therefore interfere. It cannot be too strongly emphasised that the indiscriminate use of either of these summaries for correlation work without reference to the detailed work on which they are based can only lead to error. An endeavour has been made to make the tables and discussion as complete as possible, and therefore they include many tentative, and even some rather dubious correlations which have not yet much experimental backing. They are, therefore, intended only for use in conjunction with the more detailed accounts of their origin and reliability. In both the charts and the tables a rough indication of the absorption intensity is given by the symbols (s)—strong; (m)—medium; (w)—weak and (v)—variable.

A small group of spectra have been included at the end of each of

the four parts. These have been chosen to illustrate as far as possible some of the correlations which have been discussed, and the individual assignments for the various structural units involved have been indicated on them. As before, these include some doubtful correlations inserted for completeness, and the identifications are therefore not certain in all cases. Some particularly doubtful correlations are indicated by a question-mark on these spectra. These illustrations may also be of value to workers newly entering this field, for practice purposes.

These spectra were all obtained with a Perkin-Elmer 21B double beam spectrometer equipped with a rock-salt prism. The great majority of the spectra mentioned in the text as originating in our laboratories were also obtained with this instrument, although a few were obtained with a Hilger D.209 spectrometer working as a single beam instrument.

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