FORTSCHRITTE DER CHEMIE ORGANISCHER NATURSTOFFE

PROGRESS IN THE CHEMISTRY OF ORGANIC NATURAL PRODUCTS

PROGRÈS DANS LA CHIMIE DES SUBSTANCES ORGANIQUES NATURELLES

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Infrared Spectra of Natural Products.

By **A. R. H. Cole**, Nedlands, Australia.

With 23 Figures.

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I. Introduction.

Physical methods are being increasingly applied to the solution of structural problems in the field of organic chemistry (*25*) and the use of infrared spectroscopy is standard practice in most laboratories today. The early work of COBLENTZ (*34*) indicated that the absorption of infrared light was closely related to structural factors, but it is only in the past decade that instrumental developments have allowed full use to be made of these techniques. There is no doubt today that of absorption studies in all parts of the electromagnetic spectrum, the infrared measurements are generally the most useful for structural determinations. It is true that a more complete picture of molecular structure might be obtained through the use of X-ray- (*138*) or electron- (*26, 126, 161*) diffraction, but these methods mostly remain within the precincts of the chemical physics laboratory and have not been widely applied to the solution of everyday problems of organic chemistry. In the various fields of natural product chemistry, where compounds are often isolated in extremely small amounts, seldom crystalline in the first instance, infrared methods are particularly useful.

Fast recording infrared spectrometers became commercially available in about 1946, and much of the early work to be carried out was surveyed by RASMUSSEN (*134*) in this Series. The number of infrared papers in the literature today is far too great to attempt to cover in one article but it is hoped to give a broad picture of the field and to treat particular examples in some detail in order to draw attention to different applications.

In the early stages of post-war popularity of infrared spectroscopy, there was a tendency to regard the recording of such spectra, often with little systematic control of experimental conditions, as an end in itself. However, a firm basis for the application to structure determinations was laid by such authors as R. B. BARNES, R. C. GORE, H. M. RANDALL, R. S. RASMUSSEN, H. W. THOMPSON, G. B. B. M. SUTHERLAND, and V. Z. WILLIAMS; and recent years have seen a consolidation and critical appreciation of the field rather than the emergence of many new principles.

II. Methods.

1. General.

The interaction of chemical compounds with infrared light is related to the fact that all molecules are vibrating systems with a number of discrete vibrational frequencies. A polyatomic molecule will vibrate in a complicated manner but this complex motion can be resolved into a number of simpler components called *normal* or *fundamental vibrations*, and the number of these is determined by the number of atoms in the molecule. A non-linear molecule with n atoms will have $3n-6$ normal modes of vibration ($3n-5$ if linear) and the frequencies of some of these modes are given by the frequencies of the light absorbed. It is from the assignment of these absorption bands to specific vibrating entities in the molecule that structural information is obtained.

To interact with electromagnetic radiation, and thereby give rise to an absorption band, a vibration must involve a periodic change in the dipole moment of the molecule. Symmetrical molecules have some (symmetrical) vibrations which do not cause absorption and these are called "inactive" modes. Carbon dioxide is a simple example of such a compound. This has four normal modes illustrated by the following scheme:

(a) $\overleftarrow{O}=C=\overrightarrow{O}$ Symmetrical stretching

(b) $\overleftarrow{O}=\overrightarrow{C}=\overleftarrow{O}$ Unsymmetrical stretching

(c) (i) $\overset{\uparrow}{O}=C=\overset{\uparrow}{O}$ (ii) $O=\underset{\downarrow}{C}=O$ Bending

Only two bands, corresponding to (b) and (c) are found in the absorption spectrum, since (a) leads to no overall change in dipole moment. The bending mode (c) is described as "doubly degenerate", consisting as it does of two modes of equal frequency, at right angles to one another.

The masses of atoms and the forces holding them together are of such magnitude that the usual vibration frequencies fall in the range, 5×10^{12}–1.2×10^{14} cycles/sec. This corresponds to the absorption of light of wavelengths between 2.5 and 60 microns ($1\,\mu = 10^{-3}$ mm. $=$ $=$ 10000 Å). The position of an absorption band in the spectrum is not usually designated in terms of the absolute frequency in cycles/sec. but by reference either to the *wavelength* or the *wavenumber* of the light. A certain amount of controversy has arisen in the literature as to which of these units should be used. It is the author's opinion that the

wavenumber is to be preferred since it is a frequency unit, more closely allied to the vibration frequency of the molecule under investigation than is the wavelength of the light. Furthermore, the wavenumber is much more readily comparable with Raman displacements (*85*) which are also related to molecular vibrations and hence to molecular structures. Usually, then, the terms "wavenumber" and "frequency" are taken as synonymous in the infrared field and the unit generally employed is the reciprocal centimetre (waves per cm. or $cm.^{-1}$). For converting from one system to the other there is the simple relation

$$\text{wavenumber } (cm.^{-1}) = 10^4/\text{wavelength } (\mu).$$

The main reasons why some spectroscopists have used wavelength rather than wavenumber are firstly that wavelength is generally used in ultraviolet work, and secondly that instrument manufacturers found it easier to construct spectrometers which recorded the spectrum on a linear wavelength scale because the dispersion of sodium chloride in the range $2.5–16\mu$ is much more nearly linear in wavelength than in wavenumber. In modern instruments, however, suitable cams are employed to scan the spectrum in such a way that the final record is linear in wavenumber. It is perhaps relevant to point out here that the dispersion of quartz in the ultraviolet region of the spectrum is roughly linear in wavenumber and if early workers had appreciated this fact together with the theoretical importance of frequency in relation to energy, infrared spectroscopists might have been spared a certain amount of confusion. However, in order to facilitate reading, all band positions in this paper are given in both frequency and wavelength.

The suggestion has been made (*189*) that, in order to give the unit of wavenumber a more euphonious title, and to pay a tribute to one of the pioneers of spectroscopy, it should be called the *kayser*, to be denoted by K. It is probable that this name will be universally adopted, but for the present, most journals still prefer $cm.^{-1}$

The nature of infrared work depends greatly upon the *size of the molecule* being investigated. For small molecules (*e. g.* those containing up to approximately twelve atoms), which are usually investigated in the gaseous state with spectrometers of high resolving power, the aims may be divided into three sections: (a) the assignment of the absorption frequencies to specific modes of vibration; (b) the explanation of the rotational fine structure of the individual absorption bands (leading to evaluation of the moments of inertia of the molecule, and hence to bond lengths and angles); and (c) the correlation of the vibration frequencies with a potential function which includes force constants related to the periodic changes in bond lengths and bond angles taking