Chemical Infrared Spectroscopy

W. J. Potts, Jr.

VOLUME I

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VOLUME I, TECHNIQUES

John Wiley & Sons, Inc., New York · London · Sydney

Preface

My original intention in this work was to provide in one reasonably convenient place a good share of the material with which a practicing chemical infrared spectroscopist would wish to be familiar. While its preparation was in progress, however, it became obvious that it would require far longer to complete than originally estimated and that the field of infrared spectroscopy was changing rapidly enough to make the earlier sections obsolete before the whole work was finished. Accordingly, the decision was made to present the work in two volumes, into which it naturally divides: Volume I on experimental techniques and background theory and Volume II on spectral interpretation.

This volume is essentially a synthesis of the experience of the infrared section of the Chemical Physics Research Laboratory of The Dow Chemical Company. It is not primarily intended as a textbook but rather as a practical guide to the techniques by which infrared spectroscopy is applied to the problems of chemistry. An extensive bibliography has been omitted, for references have already been supplied in other works (see, especially, Lecomte's treatise on infrared spectroscopy in *Handbuch der Physik*); selected references have been given solely for the purpose of guiding the reader to discussions on particular points more extensive than those that fall within the scope of this work. I have avoided discussion of commercial spectroscopic equipment and concentrated instead on general principles. This was possible because nearly all of the equipment in our laboratory was constructed there; all spectra and data presented in this volume have been obtained with

spectrometers designed and built by L. W. Herscher and his associates in our laboratory.

This work can only be properly described as multiauthored, for nearly all of its chapters have been influenced both generally and specifically by several people. It is a real pleasure to acknowledge their contributions:

The advice of H. D. Ruhl, A. M. Bartz, and especially L. W. Herscher has been most helpful in the preparation of Chapters 3 and 4 on infrared instrumentation.

Chapter 5, dealing with sample preparation techniques, is to a large extent the synthesis of the experience in our laboratory over many years and is the product of its many workers, both past and present. The list of contributors here is far too long to be meaningful, but to each sincere thanks are due nonetheless.

Association with N. Wright over several years provided much of the stimulation for Chapter 6 on the aspects of quantitative analysis. His pioneer work in this field is well known. My thanks are also extended to J. R. Scherer and J. Overend for discussions on the subject of integrated intensities.

The techniques of difference spectroscopy and aqueous solutions covered in Chapter 7 were originally conceived by N. Wright and have been developed and expanded by D. S. Erley.

It would not have been possible for me to prepare Chapter 8, a condensed theory of polyatomic vibrational spectra, without the patient instruction in these subjects by J. Overend and J. R. Scherer. However, full responsibility for any errors or misleading impressions belongs to me alone.

The permission of The Dow Chemical Company to prepare this work for publication and the extensive use made of their facilities are gratefully acknowledged.

The encouragement and stimulation of Professors B. L. Crawford and S. W. Fenton had much to do with the initial decision to prepare this work, and I am indebted to them for many helpful discussions and suggestions in its preparation. Continued association with them in teaching the summer infrared courses at the University of Minnesota is a rewarding and pleasant experience. The pedagogical nature of the material included herein and its order of presentation is close to the lecture material presented in this course.

I take great pleasure in thanking R. M. Hexter of the Mellon Institute for his conscientious critical review of this work while in preparation. Few authors, I think, have been so fortunate as a result of their publisher's choice of reviewer.

This work owes its principal inspiration to N. Wright, director of the Chemical Physics Research Laboratory of The Dow Chemical Company. Although he will deny it, he could and should have prepared it himself many years ago. It is a rare privilege to work in his laboratory.

The unfailing cooperation and understanding of Mrs. Joyce B. Potts during the preparation of this book has made it not only possible but a pleasant task as well.

Midland, Michigan   W. J. POTTS, JR.
July 1963

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The nature and properties of infrared radiation

Infrared radiation is usually defined as that electromagnetic radiation whose wavelength is between the limits of 0.7 and $\sim$500 μ. Radiation shorter than 0.7 μ falls in the visible region, whereas radiation of wavelengths greater than $\sim$500 μ begins to fall within the purview of those concerned with microwave radiation and can be generated by strictly electronic apparatus. Later we shall subdivide this larger region of the electromagnetic spectrum into smaller regions, and we shall see which are of most interest for chemical analysis and structure determination and why.

I. Fundamental properties of electromagnetic radiation

Since infrared light is a form of electromagnetic radiation, let us first review some of the simple fundamental properties of such radiation. An elementary understanding of it is necessary before we can proceed to describe its interaction with matter. Here, and in subsequent chapters, the results of quantum theory and other advanced concepts of physics are presented without proof; the reader is referred to appropriate texts for this material.

A. Wave nature of light

Before the quantum theory was expounded, physicists were able to explain most of the properties of light by postulating it to be an *alternating electric* field of very high frequency, which moves in the

direction of the light propagation. A moving electric field implies a moving magnetic field perpendicular to it (see any text on electromagnetic radiation); hence light radiation was pictured as a combination of an alternating electric field and magnetic field:

$$S \xrightarrow{} N$$
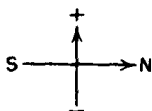
where $\uparrow$ represents the instantaneous electric vector, $S \to N$ represents the instantaneous magnetic vector, the direction of light propagation being toward the reader. Further, this electric field motion was visualized as a wave motion (sine function). The maximum points
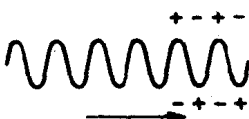
on this curve of wave motion represent the electric vector pointing upward; the minimum points represent the electric vector pointing downward. (As already mentioned, specification of the electric component of radiation implies the magnetic component; hence we shall ignore it in our discussion. It is the electric component that concerns us.)

B. Wavelength

The linear distance between two successive maxima (or minima) of the wave motion is termed the *wavelength*, usually abbreviated λ.
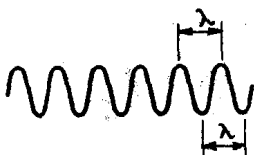
This property explained well the diffraction effects of light (see any elementary physics text) and was assumed to be a fundamental property of light radiation. The specification of wavelength was found sufficient to describe completely any type of monochromatic radiation, and the properties of a given sort of radiation could all be deduced from the statement of wavelength alone.

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C. Frequency

Another property of light radiation, which is *not* independent of wavelength, but related to it, as we shall see, is the *frequency*. The frequency of monochromatic radiation is the number of times per second that the electric vector goes through a complete cycle of direction change (from plus to zero to minus to zero to plus). The classical wave-motion concept of light defines frequency as the value of ν in the equation

$$\mathbf{E} = \mathbf{A}\sin 2\pi\nu t, \tag{1-1}$$

where $\mathbf{E}$ is the instantaneous electric vector, $\mathbf{A}$ is a vector whose length is proportional to the square root of light intensity, t is time.

D. Velocity and the relation between wavelength and frequency

All electromagnetic radiation, no matter what its wavelength or direction of propagation, moves (in a vacuum) with a constant velocity. This universal constant of nature is abbreviated c, has the value 3×10^{10} cm/sec, and is the basis for the relation between wavelength and frequency. Consider a fixed point past which radiation is moving (as a wave motion). The number of maxima passing the fixed point
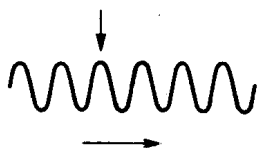
per second is the frequency, the distance between crests is the wavelength. Hence the velocity of propagation is

$$\lambda\nu = c = 3 \times 10^{10} \text{ cm/sec} \tag{1-2}$$

(λ in centimeters, ν in cycles per second). Wavelength and frequency are therefore not independent; specification of one implies the value of the other.

E. Quantum nature of light

The foregoing classical concept visualizes light radiation as a *continuous* wave motion. This postulate explained satisfactorily the properties of light radiation, except for what was known in blackbody radiation theory as the "ultraviolet catastrophy": the Rayleigh-Jeans

equation describing blackbody radiation energy, deduced from the continuous wave picture just described, predicted that the energy emitted by a body at finite temperature became large without bounds as the wavelength approached zero, clearly not in accord with experimental facts. This difficulty was overcome by Planck, who assumed that electromagnetic radiation was *not* continuous but was emitted by its source in discrete units, called quanta. Modern quantum theory predicts, and various physical experiments have consistently shown, that the *energy* of a single light quantum is given by

$$E = h\nu, \tag{1-3}$$

where E is energy in ergs, ν is frequency of the radiation in cycles per second, and h, Planck's constant, a universal constant of nature, which has the value 6.62×10^{-27} erg-sec.

The earlier results of classical physics demand a wave nature to light; quantum theory demands that light exist in discrete units, or quanta, of energy. One way to visualize radiation endowed with both these properties simultaneously is to picture a light quantum as a "wave packet," where λ, the wavelength, is the distance
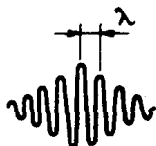
between successive maxima, as before, and the frequency ν is the number of complete cycles of electric field change per second or the number of maxima passing a fixed point per second. These "wave packets," or light quanta, move in space with constant velocity, $c = 3 \times 10^{10}$ cm/sec $= \lambda\nu$, as before.

The result of the quantum theory that we must bear in mind is that the *energy* of a quantum of light is completely specified by and is directly proportional to the frequency (equation 1-3). As we shall see, this most important relation forms the basis of interpretive spectroscopy. Had quantum theory come into being *before* light diffraction studies, it is quite likely that the use of wavelength in describing light would not have become so prevalent, frequency would have been used from the beginning in the science of spectroscopy, and there would not be the awkward situation of mixed usage of wavelength and frequency in spectroscopic practice that, alas, exists today.

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F. Units used in spectroscopy

Although wavelength units as large as the centimeter and even the meter are convenient in the radio frequency end of the electromagnetic spectrum, the optical region of the spectrum is more conveniently described in smaller units of wavelength. In the infrared region of the spectrum wavelength is usually expressed in microns, abbreviated μ; $1 \mu = 10^{-3}$ mm. Visible and ultraviolet spectroscopists commonly prefer to express wavelengths in millimicrons, mμ; 1 m$\mu = 10^{-3} \mu = 10^{-6}$ mm. In the far ultraviolet region and the x-ray region of the electromagnetic spectrum wavelength is normally expressed in Ångstrom units, Å; $1 \text{ Å} = 10^{-1}$ m$\mu = 10^{-8}$ cm.

Even in the radio frequency end of the spectrum the frequency unit cycles per second is too small and megacycles per second is commonly used. In the optical region of the spectrum the frequencies are so high that their numbers expressed in megacycles per second tend to become unwieldy. A convenient frequency unit now universally employed in optical spectroscopy is the number of waves per centimeter, or the *wave number*, as it is usually called. Consideration of the sketch on p. 3 and equation 1-2 shows that the number of waves per centimeter, ω, is

$$\omega = \frac{\nu}{c}, \tag{1-4}$$

where ν is frequency in cycles per second and c is the velocity of light, 3×10^{10} cm/sec. The dimensions of ω are centimeters^{-1}; hence ω can be expressed in units of *reciprocal centimeters*; the frequency is spoken of in "so many reciprocal centimeters," and in writing this frequency measure is abbreviated "cm^{-1}."

Equation 1-2 now becomes $\lambda \cdot c\omega = c$, or $\lambda\omega = 1$. If wavelength is expressed in microns in place of centimeters, this equation is

$$\lambda\omega = 10^4. \tag{1-5}$$

As we have already mentioned, frequency is the more useful concept for specifying light radiation, as it is directly proportional to light energy, whereas wavelength is inversely proportional to energy. The infrared literature is rapidly going over to exclusive use of frequency (in units of cm^{-1}); but many infrared spectroscopists still employ wavelength (μ), most infrared spectra are still published on a scale linear in wavelength, and upward of 70% of the infrared spectrometers sold are equipped with charts linear in wavelength. Thus

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