IR

Theory and Practice
of Infrared Spectroscopy

Herman A. Szymanski

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of Infrared Spectroscopy

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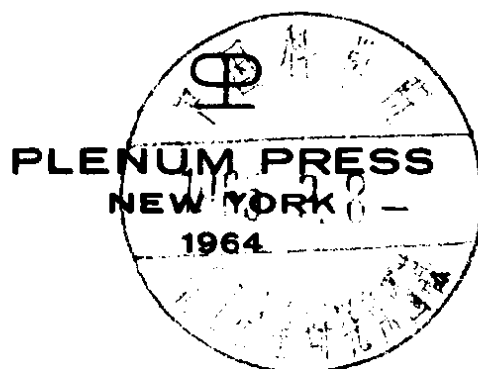
With a chapter on instrumentation by
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PREFACE

My experience with the many infrared spectroscopy institutes held at Canisius College and many discussions with both beginners and experienced practitioners in infrared spectroscopy have convinced me that there is a need for an introductory text devoted entirely to infrared spectroscopy, a text which can be utilized even by those who approach this study with only a limited background. This volume sprang from that conviction. It is intended for all who wish to use infrared spectroscopy in research — especially chemists doing structural work — in routine control work, in industrial development, or in medical applications or those military applications where it is employed as an analytical tool.

Except for the chapter on theory, the text material can be easily assimilated even by students with only the equivalent of a two-year technical degree. While it is primarily intended as a textbook for courses at either the upper undergraduate or the graduate level, this volume should also prove valuable as a reference book in the infrared laboratory.

Because I feel that the basic principles of instrument design should be understood by everyone working in infrared spectroscopy, I asked Dr. Nelson Alpert of the Perkin-Elmer Corporation to prepare the chapter on instrumentation. Dr. Alpert's wide experience in instrument design qualifies him exceptionally well for the task of writing a description of the design concepts that underlie *all* instruments in such a way that the description will not be outdated by the development of new instrument designs. I feel that he has acquitted himself admirably.

Perhaps the most difficult chapter to present was that concerned with the theory of infrared spectroscopy. To achieve a balance between a completely theoretical presentation which could be understood only by those at the graduate level and a presentation which would be so simple in approach as to have no value, I attempted to select the topics which the reader will most frequently encounter in the current literature and to explain the principles upon which each concept is based. Early drafts of this chapter were as long as the entire volume is now, and I finally decided to omit several important but not absolutely necessary topics, such as the calculation of thermodynamic parameters from ob-

served spectra. The theory of band intensity is discussed only briefly, and group theory is introduced only to illustrate some of its general applications.

I have tried to connect the qualitative aspects of group frequencies with their theoretical foundations and therefore suggest that the reader attempting to understand the interpretation of spectra combine the study of Chapter 5, which deals with qualitative analysis, with that of the theory chapter, Chapter 4.

With deep gratitude and pleasure I acknowledge the assistance of many people who have helped to make this book possible. They include Dr. Forrest F. Cleveland of the Illinois Institute of Technology and Dr. Richard Stanton of Canisius College, who made suggestions concerning the chapter on theory; Dr. Raymond Annino of Canisius College and Mr. Abram Davis of the Hooker Chemical Company, who made suggestions concerning the chapter on quantitative analysis; Dr. Frank Bajer of the Hooker Chemical Company and Dr. Ronald Erickson of Canisius College, who made suggestions concerning the chapter on qualitative analysis; and Fr. Paul McCarthy and Fr. James Ruddick of Canisius College, who made valuable suggestions for material in several chapters. Finally, many of the spectra were run by Dr. William Keiser of the Perkin-Elmer Corporation, who also offered helpful suggestions for the chapter on laboratory techniques and sample preparation.

HERMAN A. SZYMANSKI

November 1963
Buffalo, New York

In writing the chapter on instrumentation, my prime objective was to focus on information which (a) relates to operation of an instrument in obtaining useful results and (b) contributes to an understanding of the instrument so as to enhance its utility. The absence of literature references in this chapter is intentional. Much of the material does not appear elsewhere in print in a framework appropriate to the philosophy of this volume.

I wish to take this opportunity to acknowledge the constructive suggestions of Dr. Van Zandt Williams and Dr. Robert C. Gore of the Perkin-Elmer Corporation. Finally, I am grateful to Dr. Herman A. Szymanski for inviting me to participate in this project.

NELSON L. ALPERT

November 1963
Norwalk, Connecticut

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CHAPTER 1

Introduction to Infrared Spectroscopy

The study of infrared spectroscopy should include not only the practical aspects of qualitative and quantitative analysis but also its theoretical basis and consideration of such phenomena as inversion doubling, Fermi resonance, etc. This text attempts to present both the practical and theoretical aspects of infrared spectroscopy in such a way as to provide the inexperienced worker in the field with the necessary background to use it as a tool, either in an industrial laboratory concerned primarily with analysis or for research in any other type of laboratory.

1.1. FREQUENCY, WAVELENGTH, AND ENERGY OF ELECTROMAGNETIC RADIATION

In order to describe various regions of the electromagnetic spectrum, it is first necessary to present the relations that exist between the wavelength, frequency, and energy of electromagnetic waves. The relationship between *frequency* and *wavelength* of electromagnetic radiation is given by

$$\lambda v = c \qquad (1\text{-}1)$$

where

$$\lambda = \text{wavelength}$$

$$v = \text{frequency}$$

$$c = \text{velocity of light}$$

The relationship between *frequency* and *energy* is given by

$$E = hv \qquad (1\text{-}2)$$

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where

$$E = \text{energy}$$

$$h = \text{Planck's constant}$$

Let us consider specific examples of how these equations are used. Wavelength can be expressed in a variety of units, all of which can be referred to the basic unit, the *centimeter* (cm). The units most commonly employed in the ultraviolet region are the *angstrom* and the *millimicron*, while in the infrared region the *micron* is usually used. These units are defined as follows:

$$1 \text{ angstrom } (\text{Å}) = 10^{-8} \text{ cm}$$

$$1 \text{ micron } (\mu) = 10^{-4} \text{ cm}$$

$$1 \text{ millimicron } (m\mu) = 10^{-7} \text{ cm}$$

Let us consider an example of how frequency is calculated from the wavelength of radiation.

Example 1

Calculate the frequency associated with a wavelength of 3μ. The velocity of light c is given as

$$c = 3 \times 10^{10} \text{ cm/sec}$$

Since $\lambda v = c$,

$$v = \frac{c}{\lambda} = \frac{3 \times 10^{10} \text{ cm/sec}}{3 \times 10^{-4} \text{ cm}} = 1 \times 10^{14} \text{ sec}^{-1}$$

An alternate way of describing the wavelength of radiation is in terms of its *wavenumber*, which is defined by the following equation:

$$\text{Wavenumber } [\text{cm}^{-1}] = \frac{1}{\text{Wavelength } [\text{cm}]} \qquad (1\text{-}3)$$

The units of wavenumber are reciprocal centimeters. The following calculation will illustrate the conversion of wavelength in centimeters to the wavenumber unit. We shall employ the symbol $\bar{v}$ to designate wavenumber for the present, although in the current literature the symbol v is customarily used for frequency in sec^{-1} as well as wavenumber in cm^{-1}.

Example 2

Calculate the wavenumber equivalent to a wavelength of 3 μ.

$$\bar{\nu} = \frac{1}{\lambda}$$

$$= \frac{1}{3 \times 10^{-4}\,\text{cm}}$$

$$= 3333.33\,\text{cm}^{-1}$$

To calculate the energy associated with a given frequency or wavelength, use is made of equation (1-2).

Example 3

Calculate the energy associated with the frequency calculated in Example 1. The value of Planck's constant is 6.67×10^{-27} erg-sec.

$$E = h\nu$$

$$= 6.67 \times 10^{-27}\,\text{erg-sec} \times 10^{14}\,\text{sec}^{-1}$$

$$= 6.67 \times 10^{-13}\,\text{erg}$$

1.2. SPECTRAL REGIONS OF ELECTROMAGNETIC RADIATION

While we shall be primarily concerned with the infrared region of the electromagnetic spectrum in this text, let us first consider the electromagnetic spectrum in general. Figure 1-1 is a schematic representation of the regions of the electromagnetic spectrum that are of interest in analysis. These may be divided into the far-infrared, infrared, near-infrared, visible, ultraviolet, and X-ray regions, using wavelength as the criterion defining the boundaries between them. This classification is somewhat arbitrary, and the student should keep in mind that in practice the boundaries are by no means well defined and application of various analytical techniques may overlap somewhat from far-infrared spectroscopy at the long-wavelength end of the spectrum to X-ray spectroscopy at the short-wavelength end.

In the short-wavelength region waves have high energy, and when a molecule absorbs radiation of these short wavelengths the energy changes occurring in it are large. X-ray spectroscopy detects the electronic transitions of inner-shell electrons that occur when this high energy is absorbed. In the ultraviolet region electronic transitions of outer-shell electrons occur, and spectra measured in this region are often referred to as *electronic spectra*.

microns				angstroms		
1000 100 50			2	10,000 4000		1000
Far-infrared region (rotational spectra and long-wavelength vibrational spectra)	Infrared vibrational–rotational region	Near-infrared region (long-wavelength electronic spectra and vibrational–rotational spectra)		Visible region	Ultra-violet region	X-ray region (inner-shell-electron transitions)
				Outer-shell-electron transitions		

Figure 1-1. The electromagnetic spectrum.

Energy transitions in the visible and near-infrared spectral regions can be either electronic or *vibrational–rotational* in nature. For most materials, the visible spectra are representative of electronic transitions while the near-infrared spectra are representative of vibrational–rotational energy changes.

The infrared region, which can somewhat arbitrarily be defined as the region from 2 to 50 μ, is representative of transitions in vibrational and rotational energy. It is this region which will concern us in this text.

The far-infrared region (at long wavelengths) is characterized by rotational energy transitions, although some vibrational transitions of low frequency may also occur in this region.

In a spectroscopy laboratory one may find instruments designed to operate in the various regions of the spectrum and, accordingly, called ultraviolet, visible, near-infrared, infrared, and far-infrared spectrophotometers. While in some respects the data that may be obtained with each of these instruments are related to data obtainable with others, our primary concern here will be with infrared spectra as measured on infrared spectrophotometers.

1.3. THE INFRARED SPECTRUM OF A COMPOUND

Generally, infrared spectra are recorded on chart paper and presented in graphic form. A number of different ways of presenting a spectrum are possible; however, they are sufficiently similar in their essential characteristics to permit us to select one example— a spectrum recorded on a commercial spectrophotometer using the standard chart paper supplied by the manufacturer, shown in Figure 1-2—for detailed examination. (Figure 1-2 will be found in a pocket on the inside back cover.)

Along the abscissa of spectral chart paper is plotted the wavelength, or some related function such as wavenumber. In the spectrum shown in Figure 1-2 both wavelength in microns and

wavenumber in cm^{-1} are shown. The ordinate of the spectrum is some function of the amount of radiation absorbed (or transmitted) by the sample at each wavelength. A spectrum is thus a graphical presentation of the amount of radiation absorbed as a function of wavelength. Commercial spectrophotometers generally scan the pertinent wavelength region and make a tracing of the radiation transmitted. A region in the spectrum where radiation is absorbed is called an absorption band. In Figure 1-2 absorption bands are seen as valleys in the spectral trace. For example, a very deep valley may be seen at 13 μ, which indicates a strong absorption band at that point. By choosing another method of presenting the ordinate of the chart paper it is possible to have absorption bands appear as peaks rather than as valleys, and spectra presented in this manner will quite often be found in the literature.

It will be seen that in Figure 1-2 the abscissa is plotted linear with respect to wavelength. It would also be possible to plot it linear with respect to wavenumber. Spectra of both types can be found. While spectra with linear wavelength plots are still quite common, with the advent of grating instruments many workers have begun to feel that plotting wavenumbers linearly is the better method of presentation. Commercial spectrophotometers can be adjusted to record spectra either way. A spectrum recorded linear with respect to wavelength appears to have different band widths when compared to the same spectrum recorded linear with respect to wavenumber when the same length of chart paper is used in each case. This is so because at short wavelengths the wavenumber intervals are closer together than at long wavelengths. For example, the wavelength interval from 2 μ to 5 μ corresponds to the wavenumber interval 5000 cm^{-1} to 2000 cm^{-1}, while the interval from 5 μ to 10 μ corresponds to the wavenumber interval from 2000 cm^{-1} to 1000 cm^{-1}. The net effect of this inverse relationship between wavelength and wavenumber is to give a crowding of the absorption bands at low wavelengths if the abscissa is a linear wavelength function. Since adjustable scan speeds and variable chart paper speeds are available on many spectrophotometers, this crowding of absorption bands can usually be eliminated. In early instruments, which used NaCl prisms as monochromators, since the resolution of NaCl is low at the short wavelengths (2–6 μ), the spectral charts were presented linear with respect to wavelength to avoid crowding of absorption bands in the more useful region where resolution was good.

The variable plotted along the ordinate of the infrared spectrogram is a function of the amount of radiation of given wavelength absorbed by the sample. The amount of radiation of one wavelength incident on the sample (P_0) can be related to the amount transmitted

by this sample (P), to the path length in the sample (b), and to the number of particles or the concentration of the sample (c) by the equation

$$\ln \frac{P_0}{P} = abc$$

where a is a constant for any given material at a given wavelength. This equation is called *Beer's law* (also the Beer–Lambert or Beer–Bouguer law), and the relationship that it presents between the amount of radiation absorbed and the concentration is used in quantitative analysis. Chapter 6 will discuss this law in greater detail. For the present discussion of the infrared spectrogram it is necessary to define two terms which may appear in different formulations of Beer's law. One, the *transmittance T*, is given by

$$T = \frac{P}{P_0}$$

The second, the *absorbance A*, is given by

$$A = \log \frac{1}{T} = \log \frac{P_0}{P}$$

Either of these terms can be used as the ordinate in an infrared spectrum since both are related to the amount of light absorbed by the sample. Thus, an infrared spectrum can be a plot of absorbance or transmittance *versus* wavelength or wavenumber, in any desired combination. In the United States, the ordinate scale is usually so arranged that, regardless whether transmittance or absorbance is used as the ordinate, absorption peaks appear as valleys in the trace. However, tracings with the scale arranged differently, and which, of course, will appear upside down compared to the customary plots, are still found in the literature, and the student should become as familiar with them as with the others.

1.4. THE INFRARED SPECTRA OF WATER AND CARBON DIOXIDE

The infrared spectra of water and carbon dioxide are discussed at this point because these two compounds are present in the atmosphere and therefore can always be considered as possible absorbers of infrared energy in the optical path of the spectrophotometer. In double-beam spectrophotometers the absorption of these two compounds in the sample beam is generally compensated for in the reference beam so that no absorption bands are recorded. However, if the reference beam is attenuated to a large extent, weak bands due to these two compounds can sometimes be detected.