

Applied Infrared Spectroscopy

Fundamentals, Techniques, and
Analytical Problem-solving

A. LEE SMITH

Dow Corning Corporation

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PREFACE

After reaching a state of apparent maturity during the 1960s, infrared (IR) spectroscopy is now in a new period of robust growth. Sparking the revived interest is a variety of sophisticated new instrumentation that has led to experiments and analyses that would have been thought impossible only a few years ago. The potential for future accomplishments is even greater; these are indeed exciting times for IR spectroscopy.

The present volume is an expanded version of a chapter written for Kolthoff and Elving's *Treatise on Analytical Chemistry*. I think that it will be useful as a separate publication, as it fills a need not met by most other monographs. It is a volume based on practical experience, stressing the fundamental concepts and limitations of analytical IR spectroscopy for the chemist. It also provides extensive literature references for those who wish to explore more deeply a particular aspect of this subject. An alternative approach, a comprehensive coverage of all aspects of IR spectroscopy in one volume, would be encyclopedic in scope; it would also be obsolete before it was printed.

In keeping with the analytical approach, only enough theory is developed to give the reader a feeling for the basic principles of molecular dynamics. Good technique is critical if one wishes to obtain the maximum information from the spectrum; computerized instrumentation cannot compensate for casual or careless manipulation of samples or spectrometer. Therefore, considerable emphasis is given to this topic. Because it is important that the user of an IR spectrometer understand how his instrument operates, the basic design principles of existing spectrometers are described briefly. Listings of references to literature spectra and to discussions and reviews of special topics should prove useful. Since quantitative analysis by IR spectroscopy seems to be an underused and misunderstood technique, it is highlighted, and several examples are given to illustrate a variety of quantitative analyses. Factors affecting group frequencies are reviewed, but individual group frequencies are not discussed in great detail, first because excellent treatments of this topic are already available, and second because it is the author's conviction that overreliance on tables and charts, to the exclusion of the study of reference spectra, is a mistake. Because this book is analytically oriented, not discussed are a number of interesting topics that seem to fall more

in the realm of physical chemistry—although the dividing line between analytical and physical chemistry is admittedly a hazy one. Not included are such topics as chemisorption and the mechanism of heterogeneous catalysis, studies of molecular structure, rotation-vibration spectra analysis, and the determination of energy-band separation in semiconductors.

Throughout the book fundamental concepts and limitations are stressed, so that the reader is provided with a sound basis for pursuing his own more specialized interests.

It is customary and appropriate to thank those who have contributed to such a work as this. I have had the good fortune to know and to have worked with some of the best applied spectroscopists in the world. To them I owe a great deal, for their instruction, advice, and encouragement. I would particularly like to acknowledge the help of Clara Craver, Peter Griffiths, N. J. Harrick, R. W. Hannah, and R. A. Nyquist, who have read portions of the manuscript and offered helpful comments. Finally, I would like to thank Miss Gertrude Binder and Mrs. Myrna Freeman for their dedicated effort in typing the manuscript.

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CHAPTER

1

INTRODUCTION

SCOPE OF IR

Infrared spectroscopy (IR) is used by workers in many disciplines, but the term carries a different meaning in each field. To the analytical chemist, it is a convenient tool for solving problems such as determination of the five isomers of hexachlorobenzene; characterization of the wax, resin, polymer, and emulsifier in emulsion polishes; and identification of the country of origin of illegal opium. To the physicist, it may represent a method for studying energy levels in semiconductors, determining interatomic distances in molecules, and measuring the temperature of rocket flames. To the organic chemist, it furnishes a way of fingerprinting organic compounds, picking out functional groups in an organic molecule, and following the progress of a reaction. To the biologist, it promises a method of studying transport of bioactive materials in living tissue, provides a key to the structure of many natural antibiotics, and gives many clues in the study of cell structure. To the physical chemist, it can furnish a revealing look at mechanism of heterogeneous catalysis, provide a convenient means for following the kinetics of complicated reactions, and serve as an aid to determining crystal structures. In these fields and many others, IR spectroscopy provides researchers with powerful insights. It is probably fair to say that IR spectroscopy is the most nearly universally useful of all instrumental techniques.

HISTORY

The existence of IR radiation was first recognized in scientific literature in 1800 by Sir William Herschel [3], who used a glass prism with blackened thermometers as detectors to measure the heating effect of sunlight within and beyond the boundaries of the visible spectrum. Although Herschel first concluded that IR radiation was of the same nature as visible light, he later reversed his belief because of the two different curves he obtained for "luminosity" and heating effect. Herschel's main interest was astronomy, however, and he did not further investigate the "heat spectrum."

Interest in this phenomenon lay dormant for the next 80 years, but during 1882–1900 several investigators, using the comparatively crude methods available to them, made brief forays into the IR region. Abney and Festing [1], for example, photographed absorption spectra for 52 compounds to $1.2\text{ }\mu\text{m}$ and correlated absorption bands with the presence of certain organic groups in the molecule. Julius [5] investigated the spectra of 20 organic compounds using a rock-salt (NaCl) prism and bolometer detector. He found that compounds containing a methyl group absorbed at $3.45\text{ }\mu\text{m}$, but his measurements at longer wavelengths were grossly in error.

The theory of IR absorption had not yet been developed, and up to that time it was by no means settled whether the absorption was due to the presence of individual atoms within the molecules, to intermolecular effects, or to intramolecular motions. Julius' work indicated that the latter explanation held, specifically, that the grouping of atoms in a chemical composition determines the absorption pattern.

Activity in the field was growing, but it remained for W. W. Coblentz to lay the real groundwork for IR spectroscopy. During his classic researches starting about 1903, he investigated the IR spectra of hundreds of substances, both organic and inorganic [2]. His work covered the rock-salt region with a thoroughness and accuracy such that many of his spectra are still usable today.

The experimental difficulties of the early researchers were enormous. They not only had to design and construct their own instruments but all the components as well. This included grinding and polishing the prism, silvering the mirrors, and constructing the radiometer. The instruments were calibrated by using values for the indices of the refraction of rock salt measured by themselves or other investigators. Spectrometers were usually located on the basement floor and measurements often made at night, to minimize the effect of vibrations on the sensitive radiometer or radiomicrometer. Since each point in the spectrum had to be measured separately and at least 10 points per micrometer were measured, obtaining a spectrum was a tedious job requiring 3–4 h or more [4].

Out of this early work came the recognition that each compound had its own unique IR absorption pattern and that certain groups, even in different molecules, gave absorption bands that were found at approximately the same wavelength. Because of the difficulty of measuring the spectra, however, the technique was virtually unused by chemists until the 1940s.

World War II brought not only an expanded need for analytical instrumentation, but also a rapid advance in the science of electronics. It became possible to amplify electronically the very small signals obtained

from a tiny thermocouple in an IR spectrometer and to record them on a strip chart. Because the thermocouple was slow in response, a direct-current (DC) signal was used and drift was a serious problem. Nevertheless, with luck and care, spectra of quite good quality could be obtained in a matter of 1-2 h.

The next significant improvement came with the technique of making thermocouple detectors with response rapid enough for them to be used with radiation that was chopped five to ten times a second. This advance made possible elimination of drift in the spectrometer record and opened the door to the possibility of double-beam spectrometers, which could be programmed to give charts reading in percent transmittance as a function of linear wavelength or wavenumber [7].

This development took IR spectroscopy out of the realm of tedium, and as chemists became aware of its potential, popularity of the technique expanded rapidly. After a period of intensive effort during which thousands of materials were examined and instrumental limitations explored, spectroscopists began to demand better resolution and wavelength accuracy. Grating dispersion answered at least some of these demands, and with the advent of interferometer spectrometers, the possibility of obtaining accurate band contours in liquids and solids is now in sight. Perhaps it is not too much to hope that it will soon be possible to obtain noise-free spectra that truly represent the contours, frequencies, and intensities of the molecular absorption pattern, undistorted by spectrometer or sample cell artifacts.

APPLICABILITY

The IR absorption spectrum of a compound is probably its most unique physical property. Except for optical isomers, no two compounds having different structures have the same IR spectra. In some cases, such as with polymers differing only slightly in molecular weight, the differences may be virtually indistinguishable but, nevertheless, they are there. In most instances the IR spectrum is a unique molecular fingerprint that is easily distinguished from the absorption patterns of other molecules.

In addition to the characteristic nature of the absorption, the magnitude of the absorption due to a given species is directly relatable to the concentration of that species. Thus measurement of absorption intensity gives, on simple calculation, the amount of a given constituent present in the sample.

The technique is almost universal in scope. Samples can be liquids, solids, or gases. They can be organic or inorganic, although inorganic materials sometimes do not give very definitive spectra. The only mole-

cules transparent to IR radiation under ordinary conditions are monatomic and homopolar molecules such as Ne, He, O₂, N₂, and H₂.

Another limitation is that the ubiquitous solvent water is a very strong absorber and, furthermore, attacks ordinary rock-salt sample cells. Infrared is usually not very sensitive to impurities in a sample at levels below 1%. This can be a blessing or a curse, depending on one's viewpoint and the problem at hand. Similarly, the fact that positions of the characteristic absorption maxima for different groups are not quite constant from one molecule to another may be frustrating, but it accounts for the uniqueness of the absorption pattern and furnishes more clues to molecular structure than if the bands were invariant.

Spectroscopy in the IR region has some special difficulties. Because the radiation is invisible, optical materials cannot be evaluated by the eye. The energies involved are extremely low and become lower at longer wavelengths.

As a consequence of this low energy, the signal from the detector is not very much greater than the noise arising from random thermal motions of electrons within the detecting circuit. Furthermore, since all the components of the spectrometer are warm (compared to the absolute zero) and thus radiate IR energy, large amounts of false radiation reach the detector and must be distinguished from the true signal. Someone has said that IR spectrometry is roughly comparable to photographing an emission spectrum using a white-hot spectrograph. In view of these difficulties, Dr. Samuel Johnson's comment comparing women preaching to dogs walking on their hind legs might aptly apply to the obtaining of spectra by the early IR pioneers; it was not done very well, but one is surprised to find it done at all.

SELECTION OF AN ANALYTICAL TECHNIQUE

As a general rule, IR spectroscopy should be used wherever specificity is desired. A melting point, refractive index, or specific gravity gives only a single point of comparison with other substances. By contrast, an IR spectrum gives an almost infinite number of such points. It usually furnishes a more definitive test for functional groups than does chemical analysis.

Infrared is usually to be preferred when a combined qualitative and quantitative analysis is required. Applications of this type include following organic reactions, particularly when the course of the reaction is not well known, and characterizing the end products of such reactions.

The IR approach is indicated in quantitative analysis of complex non-

volatile mixtures such as polymers or in the cases where separation of components of a mixture is difficult using gas chromatography (GC).

On the other hand, the IR spectrum will not show differences in composition or structure that are reflected in the spectrum as variations of the same magnitude as random instrumental errors. It will not indicate whether a material will meet performance specifications, except as performance can be related to the presence or absence of certain absorption bands. As with any complex data, the spectrum is capable of being misinterpreted by persons who have only a superficial knowledge of the field.

Other techniques may be faster or more specific in certain areas. For example, nuclear magnetic resonance (NMR) can often furnish more information about certain kinds of soluble organic molecules without reference spectra or standards. Standards are less important in mass spectroscopy, and smaller samples may be used, but the material must be volatile and the range of applicability is somewhat less than for IR. Gas chromatography, mass spectroscopy, and ultraviolet (UV) all give excellent sensitivity for trace analysis within their limitations. Again, for certain materials, these three techniques are capable of giving excellent quantitative results. Raman spectroscopy may be used for analytical purposes in a manner similar to IR but is more often complementary than competitive [6]. Thus the implication is clear that the analyst should recognize the capabilities and limitations of all available techniques.

DEFINITIONS

Each branch of science has its own language, and it may be helpful here to define some of the terms that are used in the present work.

A spectrum may be regarded as an arrangement of electromagnetic radiation ordered according to wavelength. These wavelengths may range from 10^{-12} mm to millions of meters. For convenience, the terms angstrom unit (\AA) = 10^{-8} cm and micrometer (μm), formerly micron (μ), = 10^{-4} cm are used. A term often encountered in IR spectroscopy is wavenumber (ν), whose relationship to the wavelength λ is $\nu(\text{cm}^{-1}) = (10^4/\lambda)$ (micrometers). The wavenumber may be visualized as the number of integral wavelengths of electromagnetic energy per centimeter (Fig. 1.1). Wavenumber is directly proportional to energy and to the frequency of the vibrating unit emitting the radiation:

$$\sigma = \frac{f}{c} = \frac{E}{hc} = \frac{1}{\lambda_{\text{vac}}} = \frac{\nu}{n} \quad (1.1)$$

where σ = vacuum wavenumber in cm^{-1} ; f = frequency in seconds

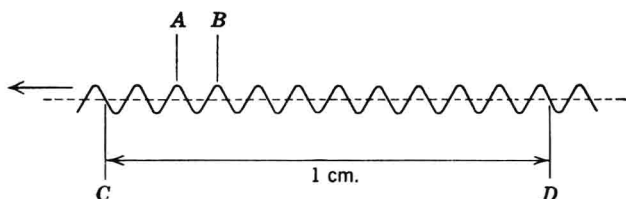


Fig. 1.1 Relationships of units. Wavelength corresponds to distance AB ; wavenumber is number of waves per centimeter, CD ; and frequency is the number of waves passing fixed point C in unit time.

(physicists often use $\bar{\nu}$ to represent frequency, but we use f to avoid confusion with the wave-number symbol ν); E = energy in ergs; h = Planck's constant; λ_{vac} = wavelength in centimeters measured in (or corrected to) vacuum; and n is the refractive index of air. From a fundamental standpoint it is more significant to speak in terms of frequency or vacuum wavenumber, since the wavelength of radiation depends on the refractive index of the medium in which it is measured. Frequency, on the other hand, is independent of the medium through which the radiation is passing.

The IR region of the spectrum is usually considered to start near the red end of the visible spectrum at the point where the eye no longer responds to dispersed radiation (thus *infra*, or below, the red), which is about $14,000 \text{ cm}^{-1}$ (7000 \AA or $0.7 \text{ }\mu\text{m}$). The so-called fundamental IR region begins at about 3600 cm^{-1} or $2.8 \text{ }\mu\text{m}$. The analytically useful IR region extends from 3600 cm^{-1} to somewhere around 300 cm^{-1} or $33 \text{ }\mu\text{m}$. This book is primarily concerned with the mid-IR, although the "near" IR region between $14,000 \text{ cm}^{-1}$ and 3600 cm^{-1} is also considered briefly. The "far" IR region is not easily defined but approximately covers the 300 cm^{-1} to 20 cm^{-1} span. It is not used much for analytical purposes. Radiation at frequencies lower than 20 cm^{-1} ($500 \text{ }\mu\text{m}$) is classified as being in the microwave or radiowave region.

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