Infrared Absorption Spectroscopy
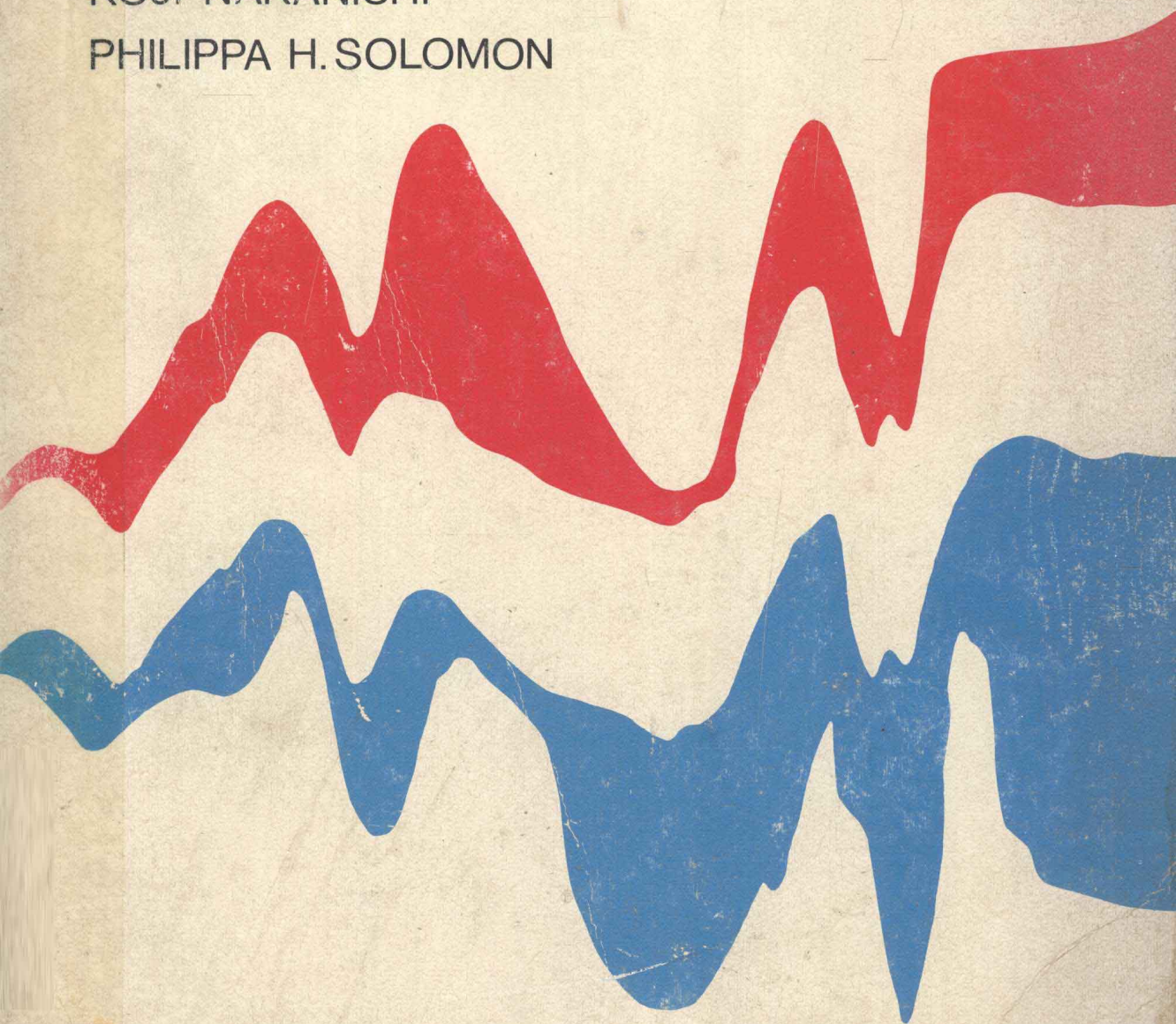
second edition

KOJI NAKANISHI

PHILIPPA H. SOLOMON

INFRARED ABSORPTION SPECTROSCOPY

—Second Edition—

≈

Koji Nakanishi
Professor of Chemistry
Columbia University

Philippa H. Solomon
Lecturer
Douglass College, Rutgers University

FOREWORD

It is not often that one has the opportunity of writing a foreword for a book fifteen years after having first encountered it. It is with relish, pride and pleasure that I do so now.

When I first saw Professor Nakanishi's original Japanese version of his "Infrared Absorption Spectroscopy" monograph in the late 1950's, IR was still the most widely used physical method of the organic chemist, NMR spectroscopy having entered the organic chemist's armamentarium only a few years before. I encouraged him to prepare an English version because I felt that he had accomplished a rare feat—the production of a small, easily readable monograph that could be used by a student as well as a practicing chemist to learn and appreciate by himself the scope and subtleties of IR spectroscopy. The large collection of problems with associated solutions in the appendix greatly added to the "self teaching" utility of the book. It was not surprising, therefore, that when the English version appeared in 1962 it proved to be an immediate success.

Fifteen years have intervened and much has happened in organic chemical methodology, notably in the use of physical methods. Proton NMR spectroscopy and mass spectrometry have become powerful routine tools and CMR spectroscopy is about to become equally widely used. Present day organic chemists, especially those who entered graduate school during the past ten years, have a tendency to use NMR and mass spectrometry almost indiscriminately without realizing that much useful and sometimes unique information can be gathered from older well-established methods, such as infrared spectroscopy. The appropriate instrumentation is considerably less expensive and its availability ubiquitous; furthermore, the instrument is very easy to operate and with relatively little practice interpretation of the data can be accomplished easily by the user himself.

It is high time that the tendency of always resorting only to the most recent and frequently also most expensive technique is counterbalanced by a critical presentation of older and time-tested methods. Infrared spectroscopy is an example *par excellence*, and having Professor Nakanishi—an internationally recognized authority in IR as well as NMR and chiroptical methods—make this case is particularly persuasive. The new edition of his book represents a fairly complete revision of the original text together with a new chapter on laser Raman spectroscopy as well as many new problems. I expect it to receive as enthusiastic a reception as the original version, and I only hope that fifteen years from now I shall again have the opportunity of writing a foreword for the third edition.

Stanford University
March, 1977

Carl Djerassi

PREFACE

For the effective usage of infrared spectroscopy in qualitative problems, it is important to become acquainted with the appearance as well as the range of absorption of the various characteristic absorption bands. The simplest way to achieve this is naturally to become familiar with actual curves. This book is set up as follows to accomplish this purpose. After a short introductory chapter, Chapter 2 presents tables of qualitative data. These are followed by Chapters 3 and 4 describing the factors that influence band positions and intensities. To supplement and enlarge on the material presented in the tables, the problem section gives a wide variety of curves to be analyzed. The answer section gives assignments of individual bands as well as interpretations of curves.

Circled figures in the "Figs." column of tables denote the problem number in which the particular band can be found.

The figures in parentheses following explanations of respective bands in the answer section refer to the standard range of absorption of that group.

The infrared and nuclear magnetic resonance data are complementary in the detection of groups. For example, the various methyl groups such as *gem*-dimethyl, methoxyl, and N-methyl are more easily detected by NMR, and accordingly a table of chemical shifts has been added (Appendix).

The book was first published in Japanese in 1960 (Nankodo, Tokyo). The qualitative section of the present book is a translation with minor revisions, while the problem and answer sections have been largely rewritten with free inclusion of curves from the IRDC Cards (cf. p. 9).

I wish to acknowledge the great help provided by the comprehensive standard texts by Bellamy, and Jones and Sandorfy. A great deal of information was also derived from the articles contributed by many authors to the "IR Spectra" (cf. p. 8).

I am very much indebted to Professors D. H. R. Barton and C. Djerassi, under whose suggestion I undertook publication of this English version. I wish particularly to extend my warmest thanks to Professor Djerassi for contributing a Foreword.

I am deeply indebted to all of my colleagues here for generous donation of time and effort, especially to A. Terahara who spent the hot summer vacation proofreading, to Mrs. J. Inoue and Miss K. Takahashi for their help in typing the manuscript, and to Phillip A. Hart, Stanford University, for reading the proofs and checking the English. Although Japanese wives are usually not acknowledged,

I think the time is ripe for this custom to be changed; I thus thank my wife Yasuko for handling expertly the noise in central Japan.

Thanks are due to the Infrared Data Committee of Japan for granting permission to reproduce a number of curves, and to the editors of *Annalen der Chemie, Annals of the New York Academy of Science, Bulletin of the Chemical Society of Japan, DMS Cards, Helvetica Chimica Acta, Journal of the American Chemical Society, Nippon Kagaku Zasshi,* and *Spectrochimica Acta* for permission to redraw diagrams. Finally, I thank the staffs of the Nankodo Company and Holden-Day in handling the numerous problems, for example, my laziness.

11th August, 1962
Tokyo

Koji Nakanishi

★ ★ ★ ★ ★

When the first edition of this book was published in 1962, following the suggestions of Professors D. H. R. Barton and C. Djerassi, I had no idea how it would be received by the chemical community. However, I was greatly relieved to see that it was accepted quite favorably, and for this I am very grateful. I had some thoughts of revising the book but various factors have contributed in giving me an excuse for not doing so.

I am greatly indebted to Dr. P. H. Solomon who has kindly undertaken the task of revising the first edition. The main characteristic frequencies had more or less been well identified by the early 1960's and hence although a computer search was undertaken for data updating, the bulk of the material has more or less been retained.

The major changes introduced in this edition consist of updating miscellaneous sections throughout the book, replacement and addition of tables and spectra, and addition of a brief section on Raman spectroscopy.

We are indebted to Professor C.F. Hammer, Georgetown University, for a critical review of the revised manuscript, to Professor R.H. Callender, City College of New York, for numerous discussions and suggestions concerning the Raman Chapter, to Professor B.J. Bulkin, Brooklyn Polytechnic Institute, for measurements of some of the Raman spectra, and to Professor C. Djerassi for kindly consenting to write another overgenerous foreword. Finally I thank my wife again for being a strong Japanese wife over the years.

December 31, 1976
New York City

Koji Nakanishi

It only remains for me to add my thanks to K.N. and to my husband Dan. Their forbearance and encouragement made this task far less fearsome than suggested in K.N.'s description above.

December 31, 1976
New York City

Philippa Heggs Solomon

TABLE OF CONTENTS

CHAPTER 1 / THE INFRARED SPECTRUM

The infrared spectrum is generally regarded as one of the more characteristic properties of a compound.

The range from 0.75 micron (one micron is 10^{-4} cm and is expressed by μ) to 200 microns, namely, from just outside the visible region and extending up to the microwave region, is called the infrared (Fig. 1.1). However, the so-called infrared region usually covers only the range between 2.5 and 40 to 50 μ; the shorter and longer wavelength regions are called, respectively, the near- and far-infrared regions. The far-infrared region extends out to 10 cm^{-1} and affords information mainly on vibrations involving heavy atoms or bond torsions.* However, it is still a rather specialized field.

The wavelength of infrared light is most frequently expressed in terms of wave-numbers, which are the reciprocal of wavelengths expressed in centimeter units. The unit of the wave-number is thus cm^{-1}. For example, the range 2.5~25 μ corresponds to 4000~400 cm^{-1}. Two types of spectrophotometers are available, those linear in wavelengths and those linear in wave-numbers. The wave-number unit is more widely used today.

All molecules are made up of atoms linked by chemical bonds. The movement of atoms and chemical bonds can be likened to that of a system comprised of springs and balls in constant motion. Their motion can be regarded as being composed of two components, the stretching and bending vibrations. The frequencies of these vibrations are not only dependent on the nature of the particular bonds themselves, such as the C—H or C—O bonds, but are also affected by the entire molecule and its environment. This situation is similar to that encountered in the spring-ball system in which the vibration of a single spring is under the influence of the rest of the system. "The internal motion of this system will become greater if energy is transferred to it." Similarly, the vibrations of bonds, which accompany electric vibrations, will increase their amplitude if an electromagnetic wave (infrared beam) strikes them. The difference between a molecule and the spring-ball system is that the vibrational energy levels of the

---

* J. W. Brosch, Y. Mikawa, and R. J. Jakobsen, "Chemical Far Infrared Spectroscopy," *Applied Spectroscopy Reviews,* 1, 187 (1968).
  K. B. Whetsel, "Near-Infrared Spectrophotometry," *Applied Spectroscopy Reviews,* 2, 1 (1968).

former are quantized; therefore, only the infrared beam with a frequency exactly corresponding to that required to raise the energy level of a bond will be absorbed, *viz.*, the amplitude of the particular vibration is increased suddenly by a certain amount and not gradually. When the sample is irradiated by an infrared beam whose frequency is changed continuously, the molecule will absorb certain frequencies as the energy is consumed in stretching or bending different bonds. The transmitted beam corresponding to the region of absorption will naturally be weakened, and thus a recording of the intensity of the transmitted infrared beam versus wave-numbers or wavelength will give a curve showing absorption bands. This is the infrared spectrum.

It was mentioned above that the frequencies of the respective bonds in a molecule are affected by the whole molecular environment. However, certain bonds have distinguishing characteristics: multiple bonds are stronger than single bonds, and X–H type bonds (N–H, O–H, C–H, etc.) have the especially light terminal hydrogen atoms. These correspond to springs that are especially strong or those connecting especially light terminal balls. Like the spring-ball system, the vibrations of these bonds are affected by the rest of the molecule to a relatively small extent. Thus the stretching frequencies of these specific bonds appear within a range characteristic for the respective type of bonds; collectively, they appear in the range of $3600 \sim 1500$ cm^{-1} (Fig. 1.1). The C=O stretching frequency appears between 2000 and 1500 cm^{-1} and is very sensitive to differences in structure and environment, a fact that makes the carbonyl absorptions extremely useful in organic chemistry.

In the region below 1600 cm^{-1} there appear bands due to the stretching of single bonds, C–C, C–N, C–O, C-halogen, etc., and also those due to the bending of various bonds. Single bonds have bond strengths of roughly the same order, and furthermore, they are usually linked cumulatively, e.g., C–C–C–O.
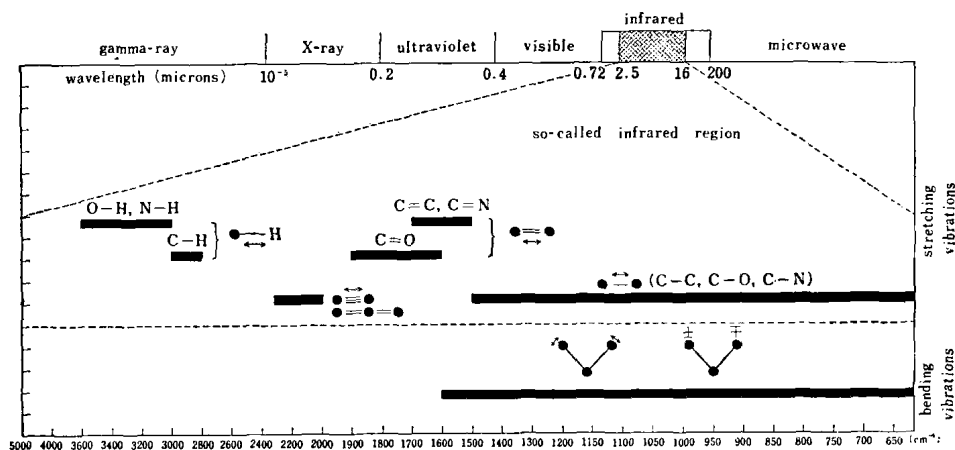

Fig. 1.1 Stretching and bending vibrations

This results in stronger mutual interaction, wider range of appearance of the bands, and great sensitivity of band positions to even minor structural changes.

The frequency range of the infrared spectrum below 1300 cm^{-1} is known as the **fingerprint region** and each compound has its own specific pattern.

However, caution must be exercised when using the fingerprint region to establish the identity of compounds, since different compounds may have very similar spectra (e.g., solution spectra of homologous fatty acids), whereas a single compound may give different spectra due to differences in sampling conditions, polymorphism, etc. (see Problem ㉕).

We shall next consider the factors that determine the position of absorption bands. The stretching frequency ν of a diatomic molecule composed of atoms with masses m and m′ can be expressed by equation (1.1)

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{f(m + m')}{mm'}} \qquad (1.1)$$

where c is the velocity of light, and f is the force constant (bond strength or bond order, corresponding to Hooke's constant of springs). The stretching frequencies of X–H bonds and multiple bonds in a larger molecule can also be approximated by the same expression. It can be seen that the position is determined by the bond strength and mass of the atoms linked by the bond. The stronger the bonds and the smaller the masses, the higher the absorption frequency of that particular bond, i.e., the more energy is required to vibrate the bond. For example, the bond strengths increase from single to double to triple bonds and the stretching frequencies also increase from 700~1500 cm^{-1} to 1600~1800 cm^{-1} to 2000~2500 cm^{-1} (Fig. 1.1). Thus a bond of higher order absorbs at higher frequency, provided the masses of the bonded atoms are identical. Also, to a first approximation, the heavier the atoms concerned, the lower the frequency. Thus the stretching vibration of the O–H bond is at 3600 cm^{-1} but is lowered to 2630 cm^{-1} in the O–D bond, where the bond strength is the same and only the mass has been increased. Qualitatively, the bending frequencies can also be treated in the same fashion.

The characteristic bands most frequently used in the interpretation of molecular structure appear within a certain range which is independent of the rest of the molecule, since they arise from bands which contain the especially light hydrogen atom or the especially strong multiple bonds. However, since individual bonds never vibrate completely independently with respect to the remaining part of the molecule, the band positions vary in a complex fashion from case to case. This variation in positions is a factor of major importance in qualitative analysis.

A vibration is not necessarily accompanied by an infrared absorption band. An absorption occurs only when the vibration causes a change in the charge distribution within the molecule. The larger the change the stronger the absorption. Accordingly, bands of hydrocarbons, which are composed only of carbon and hydrogen atoms, are weak, but bands associated with bonds connecting atoms that differ considerably in their electronegativities, e.g., C–N, C–O, C=O, C≡N, are usually quite strong. Although it was mentioned above that bending frequencies and stretching frequencies of single bonds appear in the same region, the C–O and C–N stretching bands can be detected rather easily because they are stronger than the C–C stretching bands.

Absorption bands that appear with a relatively high intensity in a range characteristic for a certain group and that are useful for the identification of that

group are called **characteristic frequencies** or **characteristic absorption bands**. A tremendous amount of data regarding these bands have been accumulated since the late 1940's and many bands in the fingerprint region are now also effective for characterizing the various groups.

Fig. 1.2 shows the characteristic absorptions of the alcoholic hydroxyl group. These bands appear no matter in what molecules the hydroxyl group is contained. The O—H stretching band (1) because of its typically high frequency, and the C—O stretching band (3) because of its intensity are especially useful for identification. The bending frequencies (2) and (4) are also employed, although seldom, for identification. However, since the vibration of a specific bond is under the subtle influence of other nearby bonds, both the position and the intensity of these characteristic frequencies are different according to the structure of the molecule and the state of measurement. For instance, the appearance of the four hydroxyl absorptions shown in Fig. 1.2 will depend on: whether the hydroxyl group is attached to a primary, secondary, or tertiary carbon atom; whether the group is free, intermolecularly hydrogen-bonded, or intramolecularly hydrogen-bonded; the strength of the hydrogen-bond, etc. Thus a comparison

Remainder of molecule

(3) C—O stretching
$1200 \sim 1000 \text{ cm}^{-1}$

(2) C—O—H bending (in-plane)
$1500 \sim 1200 \text{ cm}^{-1}$

C

O

H

(4) C—O—H bending (out-of-plane)
$650 \sim 250 \text{ cm}^{-1}$

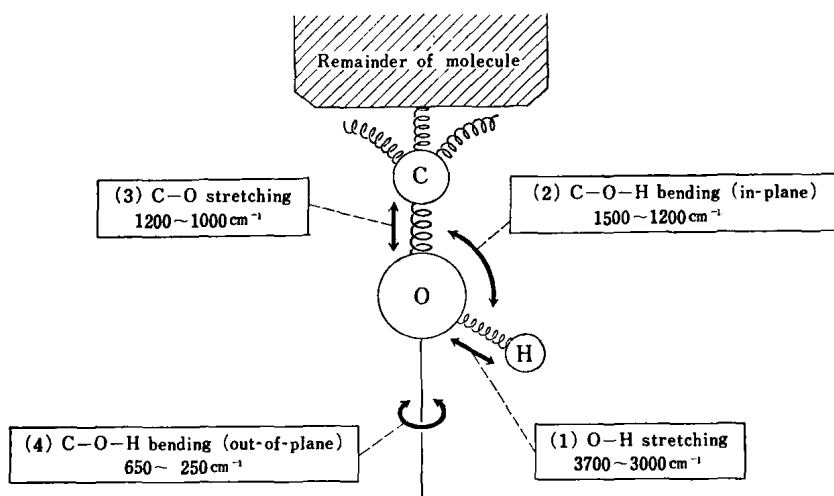(1) O—H stretching
$3700 \sim 3000 \text{ cm}^{-1}$

Fig. 1.2 Vibrations and absorptions of the alcoholic hydroxyl group.

of the bands with those of similar and known compounds would enable one to guess what sort of hydroxyl exists and in what state. This guess will be strengthened if changes in measuring conditions (solvents, etc.) or chemical structure (oxidation to ketone, acetylation, etc.) are accompanied by the appropriate changes in absorption bands. For example, if a compound having the isopropenyl group is reduced, its characteristic frequencies should disappear and instead, frequencies characteristic of the isopropyl group should appear; this would provide strong support for the preliminary assumption.

$$-C \diagup_{CH_3}^{CH_2} \quad \xrightarrow{\text{[H]}} \quad -CH \diagup_{CH_3}^{CH_3}$$
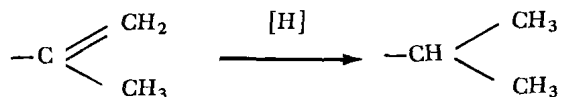
Characteristic frequencies of most groups are now known thanks to the self-recording instruments that became available in the late 1940's. These data

have been compiled in book, table, and card form and are indispensable for the identification of various groups. This **qualitative** information is one of the most important benefits of infrared spectroscopy. The absorption bands are a direct reflection of the state of molecular bonds and this aspect affords considerable information of **theoretical** interest. The band intensity is proportional to the amount of sample present and this leads to another important application of infrared spectroscopy, **quantitative** analysis.

MEASUREMENT

A polystyrene film is commonly used for calibration of wave-numbers (Fig. 1.4). An alternative is calibration using the spectrum of atmospheric H_2O (Fig. 1.3). For highly critical measurements, the International Union of Pure and Applied Chemistry (IUPAC) has formulated wave-number calibration tables based on specified mixtures of indene, cyclohexanone and camphor.‡ The cell thickness can be measured conveniently by the interference fringes (cf. Problem 1). Solvents for solids should not damage the sodium chloride cell windows and also should not react with the sample; the curves will be distorted in regions where the transmission is less than 35%. Nonpolar solvents such as carbon tetra-chloride (and carbon disulfide) are most suitable (Figs. 1.6 and 1.7), but the more polar chloroform is also widely used for its greater solvent power (Fig. 1.8). Polar solvents such as dioxane and tetrahydrofuran are employed for special purposes (Figs. 1.9 and 1.10).

Solids may also be measured as a mull with Nujol (mineral oil) or as KBr pellets. The two types of measurement are complementary since the regions obscured by Nujol absorptions (Fig. 1.5) are clear in the KBr spectra. The latter, however, usually contain bands due to adsorbed water in the regions 3300 cm^{-1} (medium intensity, O–H stretch) and 1640 cm^{-1} (weak, H–OH bend). For removal of water see p. 58).

Some tables and curves are given below.

TABLE 1.1   PRISM MATERIALS *

Material	Optimum range (μ)	Suitable range (μ)	Solubility (20°C) (g/100g H_2O)
Glass	0.3~ 2	0.3~ 2	insol.
Quartz	0.3~ 3.5	0.2~ 4	insol.
Lithium fluoride	0.6~ 6	0.2~ 6.5	0.27
Calcium fluoride	0.2~ 9	0.2~ 9.5	0.016
Sodium chloride	2~15.5	0.2~17	36.0
Potassium bromide	10~25	0.2~25	54.0
Silver chloride	2~20	0.2~22	0.00015
KRS-5 (TlBr–TlI)	2~40	1~40	0.05
Barium fluoride	0.2~13	0.2~13.5	0.17
Cesium bromide	10~37.5	1~38	124.0

* Taken from Perkin-Elmer, *Instruction Manual* 3B 9 (1954).
 The limit for usage as cell windows is at 1~2 μ longer wavelength than that shown in the Table.

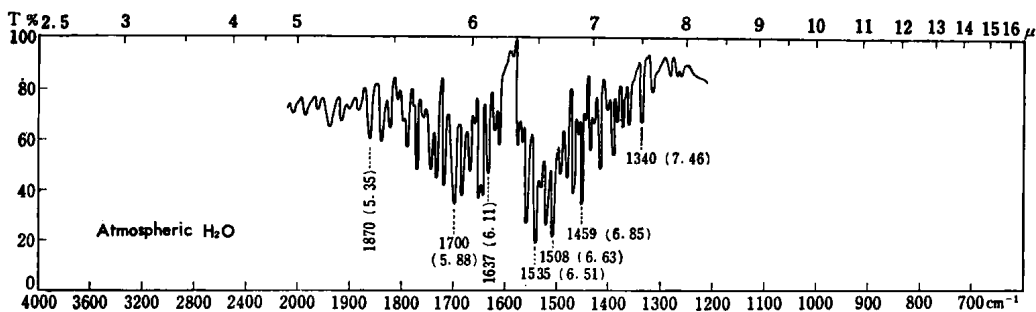‡   R. N. Jones and A. Nadeau, *Canadian Journal of Spectroscopy* 20, 33 (1975).

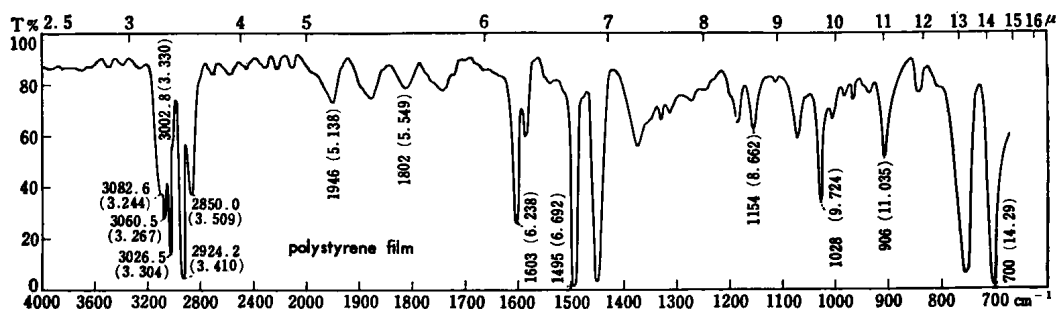Fig. 1.3 Measured by single beam apparatus. Conspicuous bands are employed for wave-number calibration.

Fig. 1.4 The wave-number is calibrated with the 3026, 3003, 2924, 1603, 1495, 906 cm^{-1}, and other bands. The film is usually mounted on a handy frame and is used also for adjusting the running conditions of the spectrophotometer.
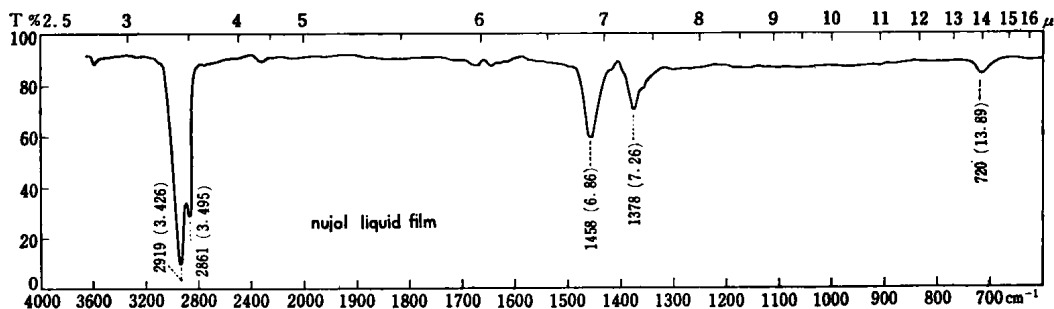

Fig. 1.5 For solid samples. Bands are due to methylene and methyl groups.
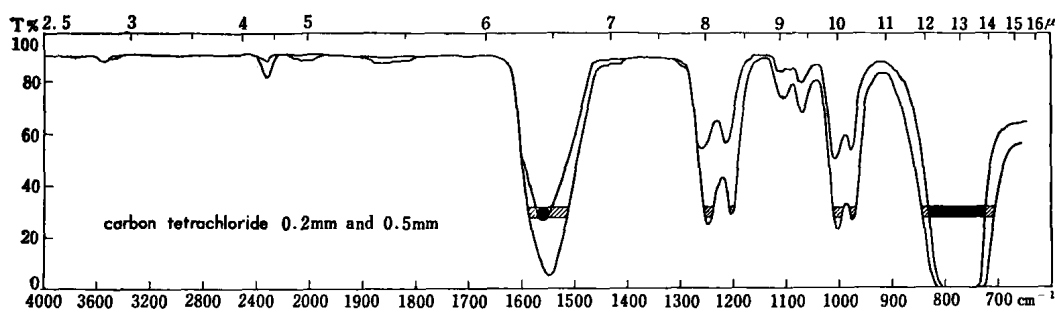
6 – *The infrared spectrum*

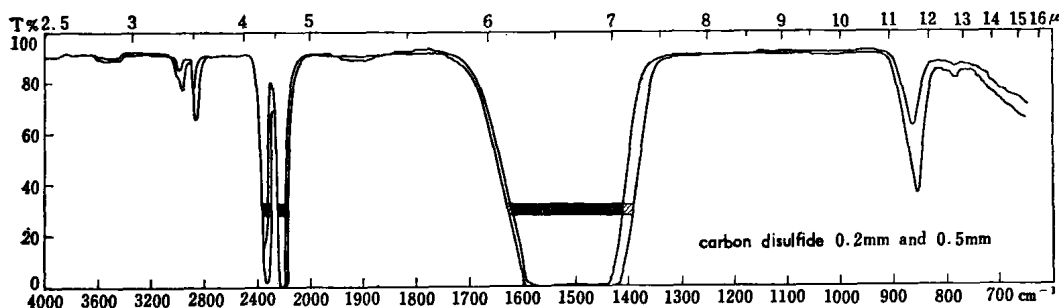Fig. 1.6*   General solvent. Specially suited for high frequency region.

Fig. 1.7*   General solvent. Specially suited for low frequency region. Best
used in a chamber because of its toxicity and inflammability. Pri-
mary and secondary amines occasionally react with carbon disulfide
to give alkyl dithiocarbamates. [R. N. Jones and C. Sandorfy,
"Chemical Applications of Spectroscopy," p. 511 (1956).]
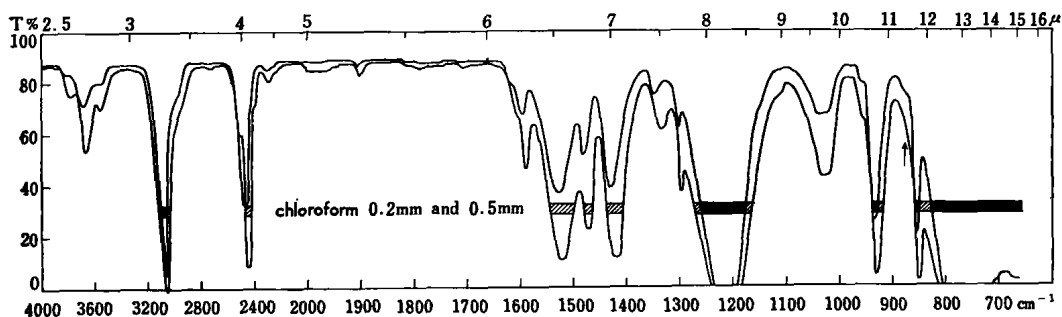

Fig. 1.8*   General solvent. Commercial chloroform contains 1~2% ethanol
as stabilizer and this can be easily detected by appearance of small
band at ca. 880 cm^{-1} (shown by arrow in Fig.). When measuring
samples that react or form hydrogen-bonds with the ethanol, the
latter should be removed beforehand by passing through alumina
or silica gel columns or other methods.‡ The ethanol-free chloro-
form can be stored for about a week; formation of phosgene is
detected by appearance of band at 1810 cm^{-1}.
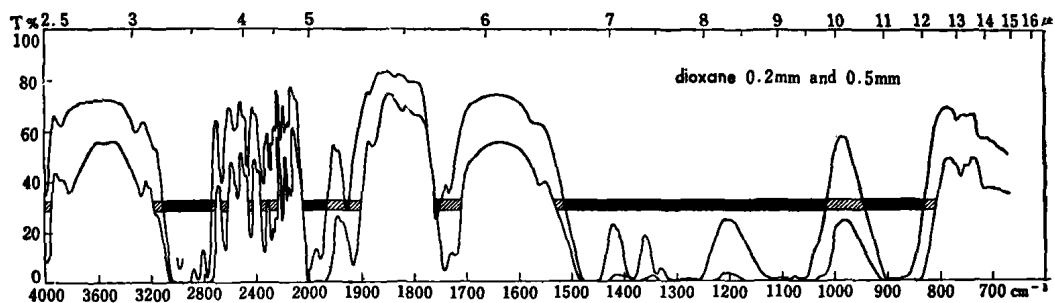
The infrared spectrum – 7

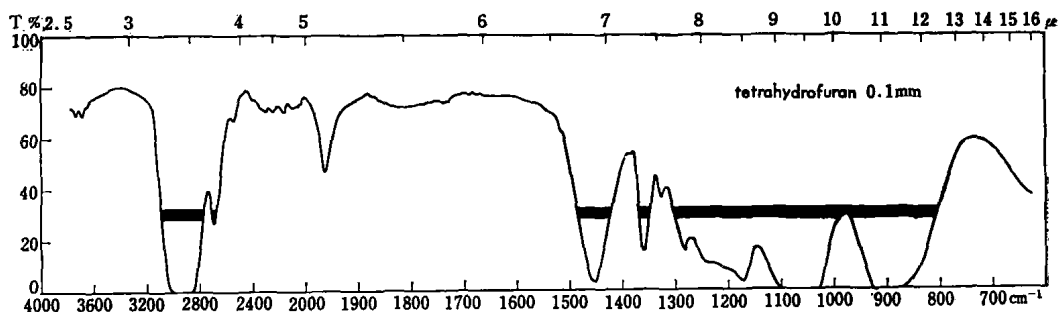Fig. 1.9* Special solvent for hydrogen-bond studies, etc.

Fig. 1.10* Special solvent for hydrogen-bond studies, etc.

CALIBRATION

For accurate calibration of prism and grating spectrometers, one should consult the following monograph.

IUPAC Commission on Molecular Structure and Spectroscopy. "Table of Wavenumbers for the Calibration of Infra-red Spectrometers," Butterworths, London, 1961.

---

* Ranges in which the percent transmission is less than 35% are shadowed in Figs. 1.6~1.10 and the respective solvents cannot be used in these particular regions.

‡ D. D. Perrin, W. L. F. Armarego and R. Perrin, "Purification of Laboratory Chemicals," p. 110, Pergammon Press, Oxford, 1966.

References

I. General

[1] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 3rd, Methuen, London, 1975.

[2] L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen, London, 1958.

[3] F. F. Bentley, L. D. Smithson and A. L. Rozek, "Infrared Spectra and Characteristic Frequencies ~700 to 300 cm^{-1}, A Collection of Spectra, Interpretation and Bibliography," Interscience, Div. of Wiley, New York, 1968.

[4] N. B. Colthup, *J. Opt. Soc. Am.*, **40**, 397 (1950).

[5] N. B. Colthup, L. H. Daly and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, 1964.

[6] N. B. Colthup, "Interpretation of Infrared Spectra," ACS Audio Course, American Chemical Society, Washington, 1971.

[7] R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Boston, 2nd ed., 1972.

[8] A. D. Cross, "Introduction to Practical Infra-red Spectroscopy," 3rd ed., Butterworth, London, 1969.

[9] K. Dobriner, E. R. Katzenellenbogen and R. N. Jones, "Infrared Absorption Spectra of Steroids," Interscience, New York, 1953.

[10] A. Finch, P. N. Gates, K. Radcliffe, F. N. Dickson and F. F. Bentley, "Chemical Applications of Far Infrared Spectroscopy," Academic Press, New York, 1970.

[11] M. St. C. Flett, "Characteristic Frequencies of Chemical Groups in the Infra-Red," Elsevier, Amsterdam, 1963.

[12] A. R. Katritzky, ed., "Physical Methods in Heterocyclic Chemistry," Vol. II, Academic Press, New York, 1963.

[13] C. E. Meloan, "Elementary Infrared Spectroscopy," Macmillan, New York, 1963.

[14] R. G. J. Miller, ed., "Laboratory Methods in Infrared Spectroscopy," Heyden, London, 1965.

[15] K. Nakamoto, "Infrared Spectra of Inorganic Coordination Compounds," Wiley, New York. 1970.

[16] J. P. Phillips, "Spectra-Structure Correlation," Academic Press, New York, 1964.

[17] W. J. Potts, Jr., "Chemical Infrared Spectroscopy, Vol. I Techniques," Wiley, New York, 1963.

[18] C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, 1963.

[19] F. Schienmann, ed., "An Introduction to Spectroscopy Methods for the Identification of Organic Compounds, Vol. I," Pergammon Press, 1970.

[20] J. E. Stewart, "Far Infrared Spectroscopy," in *Interpretive Spectroscopy*, S. K. Freeman, ed., New York, Reinhold, 1965.

[21] H. A. Szymanski, "I.R. Theory and Practice of Infrared Spectroscopy," Plenum Press, New York, 1964.

[22] H. A. Szymanski, "Correlation of Infrared and Raman Spectra of Organic Compounds," Hertillon Press, Cambridge Springs, Pa. 1969.

II. Reference Spectra

[1] Richard A. Nyquist and Ronald O. Kagel, "Infrared Spectra of Inorganic Compounds (3800–45 cm^{-1})," Academic Press, New York, 1971.

[2] Charles J. Pouchert, "The Aldrich Library of Infrared Spectra," 2nd ed., Aldrich Chemical Co., Milwaukee, 1975.

[3] ASTM — Am. Soc. for Testing and Materials, Alphabetical List of Compound Names, Formulae and *References to Published Infrared Spectra, an Index to 92,000 Published Infrared Spectra, Amer. Soc. for Testing and Materials, Philadelphia, Pa., 1969; there is also a Molecular Formula List and a Serial No. List.

[4] IRDC — Infrared Data Committee of Japan; Nankodo, Haruki-cho, Hongo, and Tokyo.

[5] SADTLER — Catalog of Infrared Spectrograms, Sadtler Research Laboratories, 3314-20 Spring Garden Street, Philadelphia, Pa.

[6] *Documentation of Molecular Spectroscopy* (DMS), Butterworths Scientific Publications, London; and Verlag Chemie GMBH, Weinheim/Bergstrasse, West Germany.

[7] API — Selected Infrared Spectral Data, American Petroleum Institute, Research Project 44, Department of Chemistry, Texas A & M University, College Station, TX 77843.