

SPECTROSCOPIC TECHNIQUES FOR ORGANIC CHEMISTS

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PREFACE

Since spectroscopy has become the main tool by which even beginning organic chemists identify compounds and study their interactions, this book has been designed to help advanced undergraduates and beginning graduate students learn these important techniques. A large number of illustrations have been included in each chapter so that students can learn in two ways, through the visual and the numerical aspects of spectroscopy, and thus reinforce their knowledge. Also included are a number of problems with solutions, so that students can test their understanding of the material as they study. Since the solutions are rather detailed, students can not only check their answers but also check their reasoning, step by step. Instructors wishing additional problems, without solutions, may consult the numerous problem books referred to at the end of each chapter.

In addition to the usual topics of infrared, proton nmr, and mass spectroscopy, this text includes a chapter on the use of the increasingly routine technique of ^{13}C nmr spectroscopy and a chapter discussing a nonmathematical treatment of the Fourier transform techniques used in modern nmr. Furthermore, we have found it useful to precede the treatment of UV spectroscopy with a brief introduction to simple Hückel MO theory, which gives additional insight into the meaning of electronic energy levels. Since timesharing computers are now an accepted part of modern college life, two timesharing versions of computer programs are included: one is for the calculation of simple Hückel energy levels, rather than deriving the hand-calculation method in detail; the other is the LAOCOON III program for the iteration of theoretical nmr spectra for a best fit with experimental spectra.

JAMES W. COOPER

*Medford, Massachusetts
February 1980*

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In undertaking a book containing hundreds of spectra, one naturally asks many favors and obtains the spectra from many sources. All of the infrared spectra were obtained on a Perkin-Elmer 727B Infrared Spectrometer running in slow scan (resolution) mode, giving a nominal resolution of 3 cm^{-1} . The water vapor and CO_2 spectrum in Figure 1.1 was provided through the cooperation of Professor Peter Griffiths of Ohio University. The spectrometer block diagram in Figure 1.4 is courtesy of Perkin-Elmer.

Almost all the proton nmr spectra were obtained from the Aldrich Library of Nmr Spectra through the courtesy of Dr. Charles Pouchert and the Aldrich Chemical Company. Many of the remaining spectra were obtained on the Tufts University Chemistry Department EM-360A and HA-100. The decoupled spectra of crotonaldehyde in Figure 4.24 were obtained through the courtesy of Bruker Instruments, Inc., of Billerica, Massachusetts. The high field spectra in Figure 4.29 were obtained by Dr. Joseph Dadok of Carnegie-Mellon University on their new 600 MHz spectrometer in correlation mode.

Most of the ^{13}C nmr spectra are plotted using a PDP-11 spectrum generation and plotting program of my own devising from data listed in the Bruker ^{13}C Data Bank, Volume 1. The remainder are actual spectra obtained on a WP-80 spectrometer at Bruker Instruments, Inc.

The mass spectra were obtained from the catalog compiled by Stenhagen et al., noted in Reference 1 of Chapter 9, and plotted using a PDP-11 plotting program of my devising on a high-precision plotter loaned to us by Dr. Ben Perlman of the Tufts Mechanical Engineering Department. Actual mass spectra were run by William Cote and Mike Santorsa of this department.

The Raman spectra in Chapter 10 were obtained by Dr. Robert Mooney and Mary Ann Hazle of the Sohio Research Center in Cleveland, Ohio.

I would also like to acknowledge the enthusiastic teaching of Professor Robert Ouellette with whom I first studied organic spectroscopy and from whom I have borrowed one or two examples, and of Professor Gideon Fraenkel who first made SHMO theory clear to me and showed me how you find the wavelength of a tennis ball. I also want to thank Professor Aksel Bothner-By for permission to reproduce the listing of LAOCOON III.

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The manuscript was typed most expeditiously by Natalie Camelo and Laurie Lydon, and the diagrams were provided by Robert Sheetz.

J. W. C.

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CHAPTER ONE

INTRODUCTION TO

INFRARED SPECTROSCOPY

IR spectroscopy is the fastest and cheapest of the spectroscopic techniques used by organic chemists. It is simply the measurement of the absorption of IR frequencies by organic compounds placed in the path of the beam of light. The samples can be solids, liquids, or gases and can be measured in solution or as neat liquids mulled with KBr or mineral oil. Thus spectra can be obtained in just a few minutes from partially purified materials in order to give an indication that the reactions have proceeded as desired.

THE IR REGION OF THE ELECTROMAGNETIC SPECTRUM

While it is common in physics to discuss light in terms of its wavelength, this is only one of two common ways of referring to IR absorptions. Let us represent the actual wavelength by λ , and recall that

$$\nu' = \frac{c}{\lambda} \quad (1.1)$$

where ν' is the frequency of the light of wavelength λ and c is the speed of light. (We are reserving ν , unprimed, to represent wave *numbers* as we will see below.) We can refer to an IR wavelength as a number of micrometers (or microns)

$$\lambda = 6.2 \times 10^{-6} \text{ cm} = 6.2 \text{ } \mu\text{m}$$

or as a frequency. We could calculate the frequency from Eq. 1.1 and find that

$$\nu' = \frac{2.99 \times 10^8 \text{ m/sec}}{6.2 \times 10^{-6} \text{ m}} = 4.82 \times 10^{13} \text{ sec}^{-1}.$$

This frequency is a large number and rather difficult to deal with, so that IR spectroscopists, recognizing that wavelength and frequency are reciprocally

2 INTRODUCTION TO INFRARED SPECTROSCOPY

related, have selected a proportionality constant such that the frequencies are numbers of a convenient size with which to work. Thus they have defined the quantity *wave number* or ν as

$$\nu = \frac{1}{(\lambda \text{ in cm})}$$

or

$$\nu = \frac{10^4}{(\lambda \text{ in } \mu\text{m})} \quad (1.2)$$

and we then find that our wavelength of $6.20 \mu\text{m}$ becomes

$$= \frac{10^4}{(6.20 \mu\text{m})} = 1613 \text{ wave numbers.}$$

The units of wave numbers are expressed as cm^{-1} or in kaysers. We thus refer to the units of wave numbers as “centimeters to the minus 1” or more commonly as “reciprocal centimeters.” Note that wave numbers are directly proportional to frequency and thus to the energy of the absorption while wavelengths are inversely proportional to energy, since

$$E = h\nu'.$$

Wave numbers are not strictly frequencies, but are proportional to frequency, and are thus commonly referred to as if they were frequencies. The actual relationship between ν and ν' is the speed of light c . If we express λ in cm,

$$\nu = \frac{\nu'}{c} = \frac{1}{\lambda}. \quad (1.3)$$

What are the frequencies or wavelengths which make up the electromagnetic spectrum? We divide light into infrared, visible, and ultraviolet in order of increasing energy, and place microwaves below and X-rays above. To compare them we will look at their relative wavelengths:

| Name | Wavelength | |
|-------------|---|-----------------------|
| | Meters | Common Units |
| Microwaves | $1 \times 10^{-1} - 1 \times 10^{-6}$ | 1 mm–10 cm |
| Infrared | $1 \times 10^{-4} - 8 \times 10^{-7}$ | 100–0.8 μm |
| Visible | $8 \times 10^{-7} - 4 \times 10^{-7}$ | 800–400 nm |
| Ultraviolet | $4 \times 10^{-7} - 100 \times 10^{-8}$ | 400–100 nm |
| X-Rays | $1 \times 10^{-8} - 5 \times 10^{-11}$ | 100–0.5 Å |

In this chapter we will be concerned only with IR frequencies, of which only the middle of the range is of interest to organic chemists. We divide the infrared region into the near, mid, and far IR as follows:

| | Near IR | Mid IR | Far IR |
|------------|---------------------------------|---------------------------|---|
| Frequency | 14,300–4000 cm^{-1} | 4000–650 cm^{-1} | 650–200 cm^{-1} |
| Wavelength | 0.7–2.5 μm | 2.5–15 μm | 15–100 μm |
| Phenomena | overtones of C–H absorptions | vibrations and bending | absorptions of ligands and other low-energy species |

ABSORPTIONS OF ORGANIC MOLECULES

The reason that most organic chemists find IR spectroscopy of great interest in their work is that most carbon–hydrogen, carbon–carbon, and carbon–oxygen bonds stretch at frequencies in the mid-IR region. Furthermore,

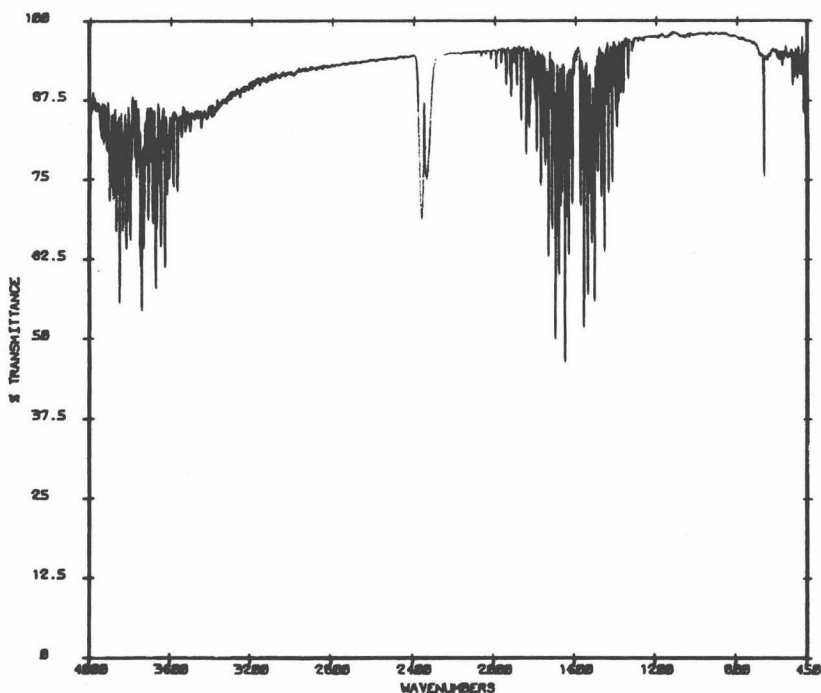


Figure 1.1 The IR spectrum of water vapor and CO_2 , showing the large number of lines due to vibrational transitions. Courtesy of Professor Peter Griffiths, Ohio University.

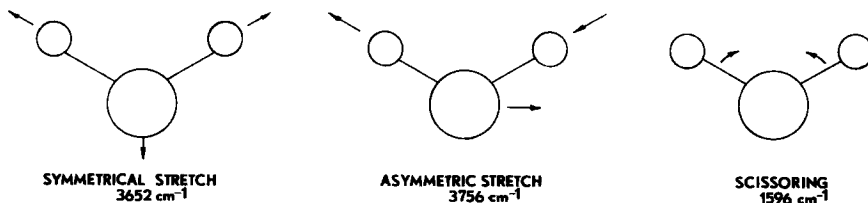
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these stretchings, rockings, and other motions are characteristic of the type of compound and of its functional groups, resonance possibilities, and shape so that the chemist can rapidly identify a number of important structural features from an IR spectrum.

If we look at a high resolution gas phase IR spectrum of some simple molecule,¹ as shown in Figure 1.1, we see that there are a veritable forest of lines stemming from the various vibrational energy levels and the smaller rotational energy levels which lie between them. These complex spectra are not amenable to simple analysis, but fortunately they are not the type of spectra with which we generally have to deal. In the liquid phase, the rotational energy levels simply broaden out the vibrational transitions, leading to a number of simpler, broad lines. These lines are characteristic of various functional groups, substitution patterns, and π -overlap as we will see below. While the lines are usually unsplit or *singlets*, we refer to related closely spaced lines as *doublets*, *triplets*, and so forth.

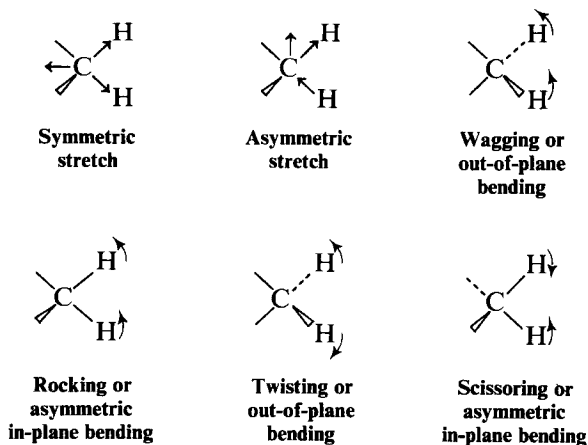
VIBRATIONAL MODES IN IR SPECTROSCOPY

Obviously, there are many possible vibrations in a molecule. However, only those stretchings which cause a change in dipole moment will show an IR absorption. Those which show no change in dipole moment may be observed by Raman spectroscopy (Chapter 10) and are often of less interest to organic chemists. To describe the types of vibrations, let us consider the simple water molecule. Since it is a bent molecule, we would expect to see various wagging and scissoring motions as common stretches. These are illustrated below:



Note that the asymmetric stretch is of somewhat higher energy than the symmetric stretch, and that both require much more energy than scissoring vibrations. These are classical stretching motions and occur exactly as drawn.

We now extend these vibrational modes to a $\text{—CH}_2\text{—}$ group, assuming that the group is anchored so that only the C and the two H's are actually in motion. Clearly other groups attached to the CH_2 affect the nature of the stretching which actually occurs.



Molecules also vibrate at combinations of two characteristic frequencies such as $\nu_1 + \nu_2$ and $\nu_1 - \nu_2$. These combination bands are not always clearly identified since they may be weak and/or in regions of the spectrum containing many other lines.

One interesting phenomenon which is occasionally observed occurs when a fundamental frequency is near an overtone from some other frequency. The result is an increase in the intensity of the overtone and a decrease in the fundamental. In the spectrum of cyclopentanone² shown in Figure 1.2, we

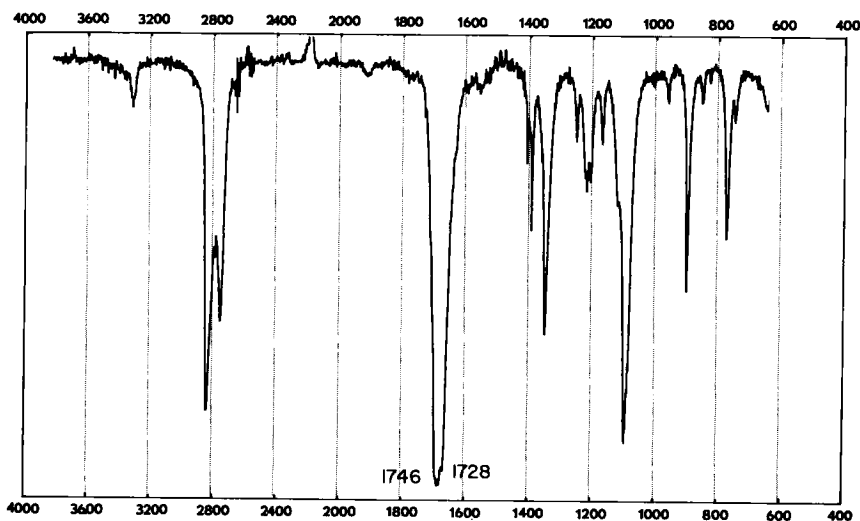


Figure 1.2 Mid-IR spectrum of cyclopentanone.