SPECTRA-STRUCTURE CORRELATION

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1964
ACADEMIC PRESS New York and London

Preface

In view of the considerable number of comprehensive volumes on spectrophotometry already available, the prospective reader may justifiably wonder what prompted the production of this small volume.

The principal novelty of this book is its attempt to present a balanced survey of the data of absorption spectroscopy for organic compounds in all regions of the spectrum from far ultraviolet to far infrared. Classification of compounds according to functional groups is the basic indexing system employed.

A second thesis of this work is that spectra in all regions permit a uniqueness of identification of a compound that is not achieved with infrared or ultraviolet data alone. As a corollary of this point the more subtle, elaborate, and word-consuming analyses of data in each region may be replaced with brief statements citing the most striking effects in several regions. This accounts in part for the brevity of the treatment.

Most volumes on spectrophotometric subjects devote most of their space to instrumentation or theory, or occasionally both. Neither topic receives more than minimum comment here because I believe that instrumental problems should be turned over to instrument specialists and not to organic chemists and that theoretical discussions of the broad spectrum considered in this volume at even a minimum level would leave no room for the data.

This is a handbook of data and a survey of it. There has been unabashed use of secondary sources, to all of which I am deeply indebted.

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Louisville, Kentucky
February, 1964

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Introduction

At a reasonable guess the number of compounds for which absorption spectra in some region have been published in the last twenty years is at least 200,000 and may be twice as many. Compilations of infrared spectra containing considerably more than 20,000 compounds and tables of ultraviolet absorption maxima for more than 50,000 compounds represent the current status of two of the continuing and successful efforts to collect current data.

The use of these vast numbers of spectra in any effective way for the characterization of molecular structure requires some sort of guiding principle. Here we have chosen to index the data according to the functional groups which are very familiar in organic chemistry, as far as this is possible.

A. Wavelength Classification of Absorption Spectra

Spectra from about 175 mμ in the far ultraviolet up to about 35 μ in the far infrared will be considered in the following chapters. Where data for all regions are available it is convenient to divide the discussion for each functional group or compound class into the following five categories, arranged in order of increasing wavelength of the absorbed radiation.

1. FAR ULTRAVIOLET

The 175 mμ lower limit is approximately the minimum wavelength obtained with a nitrogen-purged quartz spectrophotometer, and the 200 mμ upper limit is arbitrary. An occasional result from the shorter wavelengths attainable by vacuum spectrophotometers will be noted, but the ionization potentials computed from experimentation in the vacuum ultraviolet are not within the scope of the present work.

A significant part of the data below 195 mμ obtained with nitrogen-purged instruments not designed specifically for short wavelength operation is said to be invalidated by stray light effects,[1] and certainly different

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[1] T. H. Applewhite and R. A. Micheli, *Tetrahedron Letters* **1961**, 560.

instruments have been shown to yield extraordinarily large variations in the spectrum shape of a standard compound.[2]

In view of the brevity of the wavelength range representing the far ultraviolet it is not surprising that the total number of published spectra in this region is a very few thousand.

2. ULTRAVIOLET–VISIBLE

Except for relatively minor instrumental changes there is no need to distinguish the ultraviolet from the visible, and the total wavelength range for both is arbitrarily chosen as 200–750 mμ. (An official upper limit of 780 mμ has been suggested.[3])

Absorption maxima in the visible can sometimes be estimated by eye (see Table I-1). The absence of one of the wavelength groups in the table from the light transmitted by a solution normally gives the observer the impression of the complementary color, a solution strongly absorbing green light, for example, appearing purple. Since visual sensations are often complex mental interpretations of stimuli that are rarely pure transmitted light, the eye is not a reliable spectroscopic instrument. Solutions of compounds with more than one absorption band in the visible may have a misleadingly neutral appearance that changes greatly

TABLE I-1
WAVELENGTH AND COLOR

Wavelength range (mμ)	Color of light	Complementary color
400–435 or 400–450[a]	Violet	Yellow-green
435–480 or 450–480	Blue	Yellow
480–490	Green-blue	Orange
490–500	Blue-green	Red
500–560	Green	Purple
560–580 or 560–575	Yellow-green	Violet
580–595 or 575–590	Yellow	Blue
595–610 or 590–625	Orange	Green-blue
610–750 or 625–750	Red	Blue-green

[a] Different publications list slightly different ranges since the color is partly subjective and dependent on the observer.

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[2] D. W. Turner *in* "Determination of Organic Structures by Physical Methods" (F. C. Nachod and W. D. Phillips, eds.). Vol. II, Chapter 5. Academic Press, New York, 1962.

[3] Editors, *Anal. Chem.* **33**, 1968 (1961).

with illumination, concentration, thickness and other factors. Thus, aqueous solutions of chromic salts that are blue-green by fluorescent light may be red under tungsten or other types of light source. Differences of color produced by reflected rather than transmitted light are common.

3. NEAR INFRARED

The range is 0.75 μ (750 mμ) to 3 μ, though certainly the lower end overlaps the performance capabilities of most visible region spectrophotometers and the upper end from 2 to 3 μ is within the range of standard infrared instruments. However, the resolution of the salt optics used in many infrared spectrophotometers is inferior to that of the quartz prism or grating systems employed in near infrared instruments, and the latter provide better data. Perhaps it would be more nearly accurate to define the near infrared as the 0.75–3 μ range just because this part of the spectrum is conveniently measured with a photoconductive cell detector.

4. INFRARED

The salt optics region is approximately 2–15 μ (5000–666 cm^{-1}) with an occasional extension as high as 16–18 μ. Sodium chloride prisms give best results at the long end of this range of wavelengths, but the most useful part for functional group correlations is the short end. Prisms of lithium fluoride or the use of grating instruments give superior results at short wavelengths, and the present trend of commerically available models is to gratings with a vastly better performance than ever offered before.

5. FAR INFRARED

This will generally be the 15–35 μ range available to cesium bromide optics, though there are significant data to much longer wavelengths that will occasionally be cited.

The most appropriate unit for wavelength is a troublesome choice, and from the viewpoint of significant figures alone cannot be the same in all parts of the available spectrum. A decision between frequency units, which are proportional to energy, and wavelength units which are not is also required.

In the following chapters we will use the millimicron, mμ, as the unit of wavelength for the far ultraviolet, ultraviolet, and visible and avoid the wavenumber (kayser) frequency unit even though the latter is preferred by modern inorganic and coordination chemistry. For the near infrared standard practice appears to favor the micron, μ, but in the ordinary infrared the literature shows an overwhelming preference for the wavenumber frequency unit, cm^{-1}. As a result of this difference the reader may suffer some annoyance in sections of following chapters where near infrared and infrared discussions overlap. In the far infrared the micron appears to be narrowly favored over the wavenumber.

The following relationships of units may be helpful:

$$1\ \mu = 1000\ \mathrm{m}\mu = 10{,}000\ \text{Å} = 10^{-4}\ \mathrm{cm} = 10{,}000\ \mathrm{cm}^{-1}$$

B. Intensities and Shapes of Absorption Bands

The molar absorptivity, ϵ, is the nearly universal measure of light absorption for compounds of known molecular weight and is defined in terms of the Beer-Lambert law:

$$A = \epsilon bc$$

where A is the measured absorbance, b the path length of the sample in centimeters and c its molar concentration. The units for ϵ are then liters per mole per centimeter.

In general the largest values of molar absorptivity are found in far ultraviolet and ultraviolet spectra, and successful experimental work may therefore require very dilute solutions. Bands in near and far infrared spectra are commonly very feeble, and high concentrations or even the pure compounds at considerable thickness are consequently required.

The range of molar absorptivities for electronic spectra (far ultraviolet, ultraviolet–visible) is roughly 0.001 to more than 400,000, with the lower limit experimentally controlled by solubility or impurity factors and the upper limit theoretically controlled by the size of the absorbing unit and the probability of the electronic transition (see below). In the near infrared molar absorptivities of 1–10 are fairly large and values much above a hundred rare; since most of these bands are overtones and shorter wavelengths represent higher and weaker overtones, it is not surprising that the higher absorptivities usually fall at the longer wavelengths. Infrared molar absorptivities are rather infrequently calculated, but values in the hundreds are rated strong.

The molar absorptivity at a wavelength of maximum absorption may vary considerably with solvent, temperature, phase, and other factors, but the area under the whole band is often much more nearly constant and thus may be a better measure of true absorptivity. This area is the integral of $\epsilon d\nu$ where ν is the frequency. A related factor of considerable theoretical interest is the oscillator strength, f, a measure of the number of oscillators producing the absorption band; for smooth and symmetrical absorption bands in electronic spectra f may be computed from the band width, $\Delta\nu$, at half-maximum molar absorptivity by the equation[4]:

$$f = 2.2 \times 10^{-9}\, \Delta\nu\epsilon_{\max} \qquad (\Delta\nu \text{ in cm}^{-1})$$

Although the band area has theoretical significance and the molar absorptivity at a maximum does not, the latter is much easier to determine (though with a random error of perhaps 10% in the most unfavorable region, infrared).

The shape of an absorption band may be informative on occasion. For example, the measured width of the band in electronic spectra can indicate the degree of strain or distortion in a soluble complex,[5] and certainly the shape serves for the detection of overlapping or partially submerged absorptions in all regions. The numerous journals of the American Chemical Society have long banned graphs of spectral data when offered for characterization purposes only, a policy that no doubt saves space but tends to inhibit attempted analyses of band shapes.

C. Instruments

The history of spectrophotometry begins well before 1900, and rather large collections of infrared spectra by Coblentz and of ultraviolet by Jones and others before 1910 are not only pioneering ventures but very respectable work by any standard.[6] However, in the last twenty years spectrophotometry has changed its character from a research project in experimental physics to a routine technical service in many laboratories, a change due largely to the existence of commercial photoelectric spectrophotometers.

Since this book aims only at the analysis of spectrophotometric data, an indication of the approximate range, precision, and accuracy of standard commercial instruments is the only attention to instrumentation that seems justifiable.

Single instruments that can cover far ultraviolet, ultraviolet, visible and near infrared regions with only minor modifications and single

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[4] S. F. Mason, *Quart. Rev. (London)* **15**, 287 (1961).

[5] S. M. Crawford, *Spectrochim. Acta* **18**, 965 (1962).

[6] R. A. Morton, *J. Roy. Inst. Chem.* **84**, 5 (1960).

models for both infrared and far infrared are commercially available at present, and it is altogether probable that one instrument for the full range from far ultraviolet to far infrared will soon be designed.

In Table I-2 is listed a representative group of ultraviolet-visible spectrophotometers; it is evident from the wavelength ranges given that the Beckman DK's, Cary 14, Perkin-Elmer 350 and Zeiss PMQ II are the so-called "all-region" models for service from far ultraviolet through near infrared. The Beckman B and DU (both rather old models) are manual, but the others have automatic recording systems.

TABLE I-2

SPECTROPHOTOMETERS FOR ULTRAVIOLET, VISIBLE, AND NEAR INFRARED

		Accuracy	
Model	Range (mμ)	Wavelength (Å)	Photometric[a]
Bausch & Lomb Spectronic 505	200–700	5	0.005
Beckman B	320–1000	5–20[b]	0.5% *T*
Beckman DB	220–700	10–100	1% *T*
Beckman DK-2	200–3000	1[b] (uv)	0.01
DK-2A	170–3500		
Beckman DU	200–1000	0.5–5[b]	0.003[c]
Cary Model 11	200–800	<5–<10	0.004
Cary Model 14	186–2600	<4	0.002
Cary Model 15	185–800	1–10	0.002–0.005
General Electric	380–700	<10	0.5%
Perkin-Elmer 202	190–750	5–10	0.01
Perkin-Elmer 350	175–2700	1–5 (uv–visible)	—
Zeiss PMQ II	200–2500	0.5 (at 250 mμ)	—

[a] In units of absorbance except as shown.

[b] Resolution; accuracy is about half as much. In prism instruments where a range is given the lower figure is for the shorter wavelengths.

[c] L. Cahn, *J. Opt. Soc. Am.* **45**, 953 (1955).

For the infrared and far infrared there are many double beam recording spectrophotometers (Table I-3) of varying price levels and types. Many feature salt optical systems with interchangeable prisms to allow performance in more than one segment of the infrared. Combinations of prisms with gratings and of gratings with filters have been used in recent years to obtain instruments of high resolution. Accuracy to the nearest wavenumber is available in some of the newer grating models, a performance level far better than any commercial instrument could offer even five years ago, and modifications for even finer work have been successfully tried.[7] Improvements in both ultraviolet and infrared instruments are exceedingly rapid, and these tables may well be obsolete practically at the date of publication.

TABLE I-3

REPRESENTATIVE INFRARED SPECTROPHOTOMETERS

Instrument	Range (μ)[a]	Accuracy	Type
Baird NK-1	2–16+	0.015 μ; 0.5% T	Prism
Baird NK-3	2–22	1–4 cm^{-1}; 0.5% T	Prism-grating
Beckman IR 4	1–15+	0.015 μ; 1% T	Prism
Beckman IR 5A	2–16	0.025 μ; 1% T	Prism
	11–35	0.04 μ	CsBr prism
Beckman IR 7	0.7–15.5+	0.5–5 cm^{-1}	Grating
Beckman IR 8	2.5–16	0.008–0.015 μ	Filter-grating
Beckman IR 9	2.5–25+	0.2–0.6 cm^{-1}	Prism-grating
Cary 90	2.5–22	0.5 cm^{-1}	Prism-grating
Perkin-Elmer 21	2.5–15.5	1.5–20 cm^{-1}	Prism
Perkin-Elmer 137-B	2.5–15	0.03 μ; 0.5% T	Prism
Perkin-Elmer 137-G	0.83–7.65	0.004–0.012 μ	Grating
Perkin-Elmer 221	0.7–38		Prism-grating
Perkin-Elmer 301	15–167		Grating
Perkin-Elmer 421	5–40	1 cm^{-1}	Filter-grating

[a] The plus sign indicates possible range extension with an auxiliary prism.

D. Mechanisms for the Absorption of Radiation

An extensive discussion of the elaborate theoretical framework of spectrophotometry will not be attempted. Simple molecules containing only a few atoms have spectra that can be very nearly completely accounted for by suitable theories, and volumes have been written about them.[8] For more elaborate molecules a full theoretical treatment is much less likely to be available, and here only a few easy generalizations will be considered.

According to elementary quantum concepts the energy of electromagnetic radiation increases linearly with frequency. The frequencies of the infrared part of the spectrum are short and thus interact only feebly

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[7] P. J. Krueger, *Appl. Opt.* **1**, 443 (1962).

[8] G. M. Barrow, "Introduction to Molecular Spectroscopy." McGraw-Hill, New York, 1962.

with absorbing matter, effecting vibrations and rotations of molecules and submolecular groups. Rotation requires less energy than vibration and is observed in a relatively pure form in the far infrared spectra of simple compounds, but most of the ordinary infrared spectrum is associated with vibrational effects with superimposed rotational components. The near infrared is an unusual part of the spectrum in that harmonics, overtones and combinations of fundamental infrared frequencies for functional groups containing hydrogen are its most significant components (though the lower wavelength region also contains some low energy electronic transitions overlapping from the visible).

In the far ultraviolet, ultraviolet, and visible regions of the spectrum the predominant effect of absorbed radiation, because of its greater energy as compared to the infrared, is the excitation of electrons in molecules of sufficiently complex structure to have one or more such transitions needing a moderate amount of energy. Transitions requiring the least energy produce absorption bands at the longest wavelengths, sometimes reaching the lower portion of the near infrared. Vibrational components may sometimes be observed in electronic spectra in the form of fine structure, a series of closely spaced maxima that may number in the hundreds for some compounds in the vapor phase when measured with a high resolution spectrophotometer.

Compounds with absorption bands in the visible almost invariably have other bands in the ultraviolet as well, but the number of substances with ultraviolet maxima only is many times as large.

1. ELECTRONIC SPECTRA

The most common electronic transitions are indicated in the following chart (Table I-4) of electron symbols, energies, and effects. This classification, though rudimentary, is very helpful in the interpretation of ultraviolet–visible bands, as is evident throughout this volume.

Most of the $\sigma \rightarrow \sigma^*$ transitions require such high energy that they are found only below 200 mμ, in the far ultraviolet; an example is the absorption band in the vacuum ultraviolet shown by saturated aliphatic hydrocarbons. The most familiar examples of $\pi \rightarrow \pi^*$ spectra are the conjugated polyenes in which the transition energy declines with increasing length of the conjugated system and the wavelength of maximum absorption correspondingly increases. The $\pi \rightarrow \pi^*$ bands are usually strong and obviously require an unsaturated molecular structure. The $n \rightarrow \pi^*$ effects require less energy and thus appear at longer wavelengths; the weak bands of carbonyl, nitro, nitroso, and similar compounds containing both multiple bonds and nonbonding electrons on at least one atom comprising a multiple bond are very distinctive, and some of these bands are in the visible spectrum. The $n \rightarrow \sigma^*$ transition requires enough energy to appear usually at the shorter wavelengths of the ultraviolet; an example is the absorption of an alkyl halide for which nonbonding electrons are supplied by the halogen, and the maximum increases in wavelength in the order Cl < Br < I as the electrons are successively easier to excite.

TABLE I-4

Electronic Transitions and Spectra

Electron level[a]	Symbol	Transitions	Remarks
Antibonding sigma	σ^*	$\sigma \rightarrow \sigma^*$	Far ultraviolet; only transition for saturated molecules without *n* electrons.
		$n \rightarrow \sigma^*$	Usually at short wavelengths of the ultraviolet.
Antibonding pi	π^*	$\pi \rightarrow \pi^*$	Prominent in conjugated systems ("*K*-bands"); often very strong.
		$n \rightarrow \pi^*$	At relatively long wavelengths and usually weak.
Nonbonding	n		
Bonding pi	π		
Bonding sigma	σ		

[a] In order of decreasing energy from top to bottom.

There are several systems of nomenclature for electronic transitions at present. The designations "*K*-band" for a conjugated system pi-electron transition and "*R*-band" for the $n \rightarrow \pi^*$ transition are considered rather out of date. The terms $N \rightarrow V$ (sometimes the arrow is reversed) for transitions of sigma and pi electrons and $N \rightarrow Q$ for those of nonbonding electrons are often employed. Many now favor the precise designation of electron levels by letters with both superscript and subscript notations, especially for aromatic systems (see Chapter II).

The molar absorptivity of a compound is a function of the cross-sectional area of the absorbing species and the probability of the necessary electron transition. For an average organic molecule with an assumed cross-section of about 10^{-15} cm^2 a unit transition probability has been calculated[9] to correspond to a molar absorptivity of the order of

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[9] E. A. Braude, *in* "Determination of Organic Structures by Physical Methods" (E. A. Braude and F. C. Nachod, eds.). Academic Press, New York, 1955.

10^5, and the highest known values are indeed a few hundred thousand.[10] Any molar absorptivity above 10,000 is conventionally considered high and a value under 1000 low.

2. INFRARED SPECTRA

Frequencies for vibrations of individual functional groups are mostly above 1000 cm^{-1} and over-all molecular vibrations usually below this value. A summary of functional group frequencies is given in Table I-5.

The stretching frequencies for functional groups composed of two atoms, A and B, may be roughly estimated by assuming that the bond between them is a spring vibrating in accord with Hooke's law. The following equation may be used to calculate the frequency:

$$\nu(\text{cm}^{-1}) = 1307(k/\mu)^{1/2}$$

with ν the wavenumber of the band, k a force constant factor usually given the values 5, 10, and 15, respectively, for single, double, or triple bond, and μ is the reduced mass of the A-B pair in atomic weight units, $m_A m_B/(m_A + m_B)$. If A or B is hydrogen, disputed or difficult frequency correlations may sometimes be checked by substituting deuterium for hydrogen. Since deuterium is twice as heavy as hydrogen a substantial displacement of stretching frequency is calculated by the above equation; for example, the C—H stretching values are near 3000 cm^{-1} and the C—D values near 2100 cm^{-1}.

The force constant of the A—B bond is increased by substituents that tend to increase the number of electrons participating in the bond, and the result is a slight increase in the corresponding stretching frequency. Effects of this nature account for the characteristic differences of the carbonyl band position in various classes of aldehydes, ketones, and related compounds. Correlations of such frequency shifts with Hammett sigma constants,[11] group electronegativities,[12] ionization potentials,[13] chemical shifts in NMR spectra or other measures of bond polarity or electron distribution can be made with some success. Indeed, the extensive application of these correlations is one of the more important trends in recent efforts to determine structure from spectra.

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[10] J. B. Armitage, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.* **1952,** 2014; F. Sondheimer, R. Wolovsky, and Y. Amiel, *J. Am. Chem. Soc.* **84,** 274 (1962).

[11] H. H. Freedman, *J. Am. Chem. Soc.* **82,** 2454 (1960); M. St. C. Flett, *Trans. Faraday Soc.* **44,** 767 (1958); M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.* **84,** 3546 (1962).

[12] J. K. Wilmshurst, *Can. J. Chem.* **38,** 467 (1960).

[13] D. Cook, *Can. J. Chem.* **39,** 31 (1961).

In hydrogen bonded structures the functional group carrying the hydrogen must hold it more weakly than normal; thus, the force constant is effectively diminished and the absorption band is at lower frequency than for the same group with nonbonded hydrogen. Since hydrogen bonding may be intra- or intermolecular in some compounds and a portion of the hydrogens may remain unbonded, the structure of the O—H stretching region for phenols and alcohols (for example) is sometimes very informative.

When two identical A—B bonds have one atom in common, e.g.,

TABLE I-5

APPROXIMATE FREQUENCIES OF FUNCTIONAL GROUPS IN THE INFRARED

Frequency (cm^{-1})	Type of group[a]	Borderline groups
2000–5000	X—H stretching X≡X stretching Z—H stretching X=X=X stretching X=X=Y stretching	
1400–2000	X=X stretching (aliphatic) X=X stretching (aromatic) X=Y stretching	
		X—H bending X—H wagging
1000–1400	X—X stretching X—Y stretching X=Z stretching Z—H bending	
		X—X stretching X—Y cyclic
650–1000	X=X—H bending XH$_2$ rocking X—H aromatic bending X—Z stretching	
400–650	X—Z bending X—X and X—Y bending (in cyclic or aromatic compounds) X—Br stretching X—I stretching	

[a] X and Y may be carbon, nitrogen, oxygen, or fluorine; Z may be silicon, phosphorus, sulfur, or chlorine. Entries are in order of decreasing frequency.