

THEORY
and APPLICATIONS
of ULTRAVIOLET
SPECTROSCOPY

H. H. JAFFÉ and MILTON ORCHIN

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Theory and Applications of Ultraviolet Spectroscopy

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Preface

This book is an outgrowth of two courses which were given independently at the graduate level at the University of Cincinnati during the past several years. One course, "Molecular Spectra," was directed primarily to students majoring in the physical and theoretical chemistry programs. The second course, "Applications of Ultraviolet Spectrophotometry," attracted primarily graduate students in the organic chemistry program. The frequent consultations between professors as well as between students in the two courses indicated the desirability of preparing a textbook which would incorporate both theory, based on the molecular-orbital approach, and a range of applications appealing to organic chemists with a broad interest in structure determination.

The frequently successful utilization of resonance theory by organic chemists in the correlation and integration of a host of chemical facts without resort to the mathematical aspects of the theory has demonstrated the value of a working or qualitative knowledge of resonance. The application of the theory has been particularly successful in the description of molecules in the ground state. Electronic absorption spectroscopy requires not only a description of the ground state, but a knowledge and description of the excited state as well. A description of the excited state is most satisfactorily given in molecular-orbital terminology, and consistency then requires a similar description of the ground state.

The growing interest of organic chemists in understanding the molecular-orbital theory and their desire to use it as a qualitative tool served as a further stimulus to prepare a textbook in which this theory could be developed and applied.

The purpose of the book may be stated simply: to facilitate an understanding of electronic absorption spectra. In order to achieve this goal our basic problem was to organize the vast empirical knowledge of ultraviolet spectra around a framework of theoretical concepts that would neither offend the molecular spectroscopist nor appear incomprehensively complex to the great number of practicing organic chemists who desire a firm foundation for understanding and using absorption spectroscopy. Our

different backgrounds, interests, approaches, and temperaments were an advantage in the attempts to solve this problem. The principal device for effecting the necessary compromise between mathematical theory and qualitative development in this book is the use of fine-print sections. Where the logical development of certain basic concepts required a rigorous mathematical justification, this elaboration has been placed in fine print. Occasionally, descriptive material not immediately pertinent to the topic but possessing broad relevance has also been set in reduced type. The large print, then, is intended as a continuous, coherent presentation.

The book is necessarily incomplete in many respects. In order to keep the theoretical part within bounds, many of the topics not commonly encountered in experimental investigations of a nonspectroscopic nature, such as singlet-triplet absorption and spin-orbit coupling, although briefly touched upon, have not been given the space their theoretical importance might have suggested. Similarly, the profusion of experimental material has required very strong selectivity of literature references. Platt has counted as many as 500 papers on spectra appearing in a single year, and estimates indicate that about every third page in the *Journal of the American Chemical Society* contains spectroscopic information. The selections frequently have been arbitrary; familiarity with the literature, the authors' own work and interests, the desirability of developing certain thought processes—these criteria rather than complete and systematic coverage guided the selection. Material of equal or possibly greater worth may have been omitted. In the discussion of theory no specific attempt has been made to give a historical development or to distribute credit to individuals for their specific contributions; rather the primary effort was directed toward producing a unified, homogeneous picture of the present state of the theory, as far as it was believed necessary for an understanding of the experimental material. In the discussion of applications, a similar, rather arbitrary selection of references was made. The number of workers who have contributed to this picture is so tremendous that proper credit is impracticable. We sincerely hope that in this approach we have not done too many injustices to authors and work not included in this version.

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1 Light absorption and its measurement

1.1 The Electromagnetic Spectrum and Its Classification

Many apparently different forms of radiant energy such as radio waves, sunlight, x-rays, and gamma rays have similar properties, and are called *electromagnetic radiation*. All such forms of radiant energy can be considered as wave motion which travels at the same velocity (approximately 186,000 miles per second in air or 186,284 miles per second in vacuum). The wavelength, a convenient classification of electromagnetic waves, is the distance, measured along the line of propagation, between the crests or any two points which are in phase on adjacent waves. In absorption spectroscopy the wavelength, λ , is most frequently expressed in microns (μ), millimicrons ($m\mu$), or angstrom (A) units:

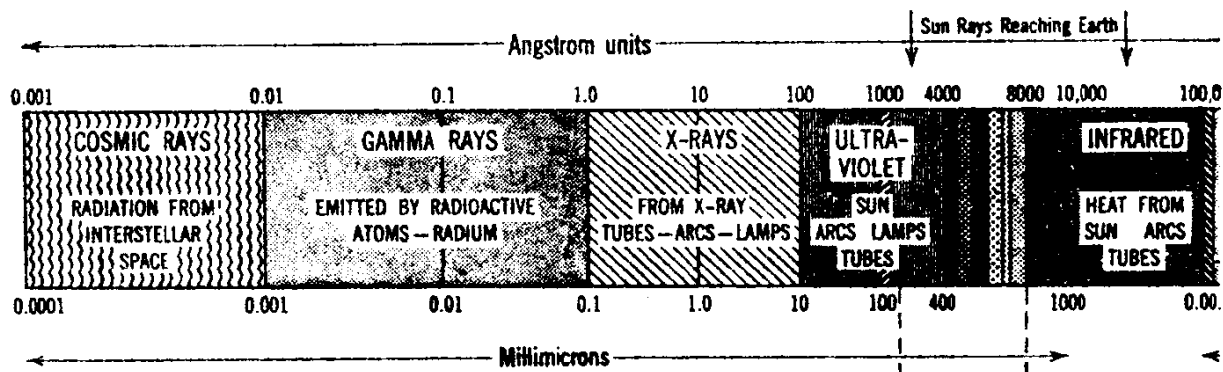
$$1 \mu = 1000 m\mu = 10,000 \text{ A}$$

The definitions of units of length have now been internationally accepted in terms of the wavelength of the red cadmium line, placed at 6438.4696 A. Thus 1 A is equal to $1/6438.4696$ of the wavelength of the red cadmium line in vacuum.

A diagram of the electromagnetic spectrum is shown in Fig. 1.1. The light of shortest wavelength is found at the blue end, that of longest wavelength at the red end, of the spectrum.

Electromagnetic radiation is classified not only by wavelength but also very frequently by the number of waves per unit distance, usually a centimeter. The number of waves per centimeter is called the *wavenumber*, $\bar{\nu}$ or $\tilde{\nu}$, and is expressed in reciprocal centimeters, cm^{-1} . The longer is the wavelength, the smaller the number of waves per centimeter: $\bar{\nu} = 1/\lambda$.

Thus a wavelength of 2000 A is equivalent to $\frac{10^8}{2 \times 10^3} = 5 \times 10^4 \text{ cm}^{-1} = 50,000 \text{ cm}^{-1}$ or 50,000 reciprocal centimeters (sometimes inaccurately called 50,000 wavenumbers). Since the magnitude of $\bar{\nu}$ in the ultraviolet



region is $>25,000$, the unit kilokayser (kK), equal to 1000 cm^{-1} is occasionally employed. Thus, in the above example

$$2000 \text{ A} \cong 50 \text{ kK}$$

The third common classification of radiation is by frequency, ν , the number of waves that pass a particular point per unit time, or the number of cycles per unit time, usually the second. In all electromagnetic waves, the frequency or number of waves passing a point per second multiplied by the wavelength equals the velocity of light (about $3 \times 10^{10} \text{ cm/sec}$):

$$\text{frequency} = \frac{\text{velocity of light (cm/sec)}}{\text{wavelength of light (cm)}}$$

The dimensions of frequency are then seconds $^{-1}$. For example, 3000 A is converted to frequency as follows:

$$\nu = \frac{3 \times 10^{10} \text{ cm/sec}}{3000 \text{ A}} = \frac{3 \times 10^{10} \text{ cm/sec}}{3 \times 10^{-5} \text{ cm}} = 10^{15} \text{ sec}^{-1}$$

Because frequencies are such large numbers in the range of wavelengths of interest to absorption spectroscopists, the unit called the *fresnel* (f) is used. One fresnel is equal to 10^{12} oscillations per second or, in the above example, $3000 \text{ A} \cong 1000 \text{ fresnels}$. In general,

$$\nu (\text{f}) = \frac{3 \times 10^6}{(\text{A})}$$

Although physicists have defined the symbol $\bar{\nu}$ to denote wavenumbers, and ν to denote frequency, in much of the literature on spectroscopy ν is used to denote *either* frequency *or* wavenumbers. The fact that frequency and wavenumbers are directly related by the equation, frequency = wavenumbers \times speed of light, probably accounts for the use of the same symbol to denote either.

The region of the electromagnetic spectrum of interest to spectroscopists extends from about 100 to 3,000,000 A. Definitions of the various regions

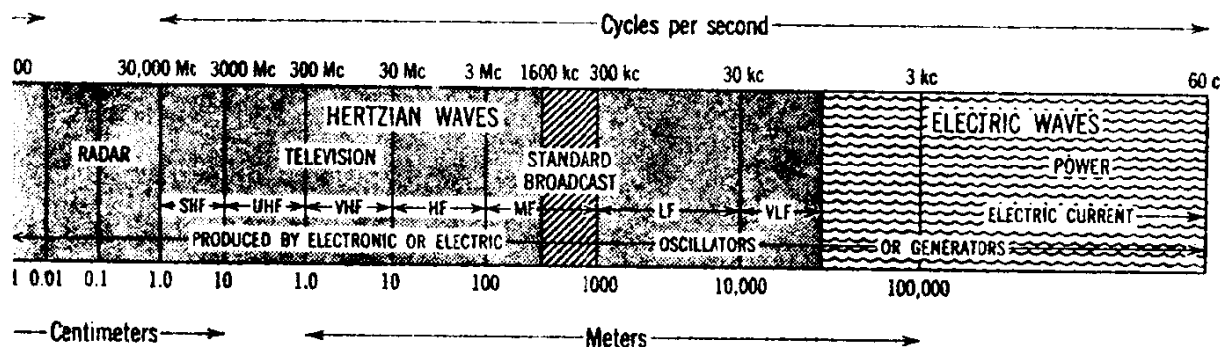


Fig. 1.1 A schematic diagram of the electromagnetic spectrum.

in this range have been proposed by the Joint Committee on Nomenclature in Applied Spectroscopy¹ and are given in Table 1.1. It is clear from this

TABLE 1
The Regions of the Electromagnetic Spectrum

Region	Wavelength		Wavenumber, cm ⁻¹	Frequency, f
	μ	\AA		
Far ultraviolet	0.01–0.2	100–2000	1,000,000–50,000	30,000–1500
Near ultraviolet	0.20–0.38	2000–3800	50,000–26,300	1500–787
Visible	0.38–0.78	3800–7800	26,300–12,800	787–385
Near infrared	0.78–3	7800–30,000	12,800–3333	385–100
Middle infrared	3–30	30,000–300,000	3333–333	100–10
Far infrared	30–300	300,000–3,000,000	333–33.3	10–1
Microwave	300–1,000,000	3,000,000–10,000,000,000	33.3–0.01	1–0.0003

listing that the use of different units in different regions of the spectrum is convenient. The adjectives near and far, when used to modify ultraviolet and infrared, relate to the visible region as a reference point. Thus the near ultraviolet is the region of the ultraviolet nearest to the visible and hence refers to the longer wavelengths in the ultraviolet region, whereas the near infrared, which describes the infrared region closest to the visible, is the infrared region of shortest wavelength.

1.2 The Classification and Origin of Spectra

EMISSION SPECTRA. When atoms or molecules are subjected to intense heat or an electric discharge, they may absorb energy and become "excited." On return to their "normal" state, they may emit radiation. Such emission is the result of a transition of the atom or molecule from a high-energy or "excited" state to one of lower energy, usually the normal or ground state. The energy lost in the transition is emitted in the form of light. Excited *atoms* usually produce line spectra, which are very valuable

¹ Report No. 6 of the Joint Committee on Nomenclature in Applied Spectroscopy, *Anal. Chem.*, **24**, 1349 (1952).

for identification purposes. Determination of the composition of celestial bodies, for example, has been aided by spectroscopic examination of their light emissions. "Excited" molecules produce band spectra. Flame spectra and arc and spark spectra are examples of such emission spectra. Other examples are fluorescence and phosphorescence spectra, which are discussed in Chapter 19.

ABSORPTION SPECTRA. When continuous radiation (i.e., light of all wavelengths) passes through a transparent material, a portion of the radiation may be absorbed and the residual radiation, when passed through a prism, may yield a spectrum with gaps in it. Such a spectrum is called an absorption spectrum. During the absorption process the atoms or molecules pass from a state of low energy (the initial or ground state) to one of higher energy (the excited state).

According to the laws of classical mechanics governing the energies of moving bodies, no restrictions are placed on the energy content of molecules or atoms. Application of these laws would lead to the conclusion that energy can be absorbed in any arbitrary quantity, and, accordingly, that all substances should have continuous spectra. However, the experimental evidence is contrary to this prediction, and the Bohr theory (named for the Danish physicist Niels Bohr) was developed to account for the fact that energy changes produced by light absorption occur only in integral multiples of a unit amount of energy called a *quantum*, which is characteristic of each absorbing species.

In both emission and absorption spectra, the relation between the energy changes in the molecule and the frequency of the light emitted or absorbed is given by the so-called Bohr condition:

$$h\nu = E_f - E_i$$

where h is Planck's constant, ν is the frequency, and E_f and E_i are the energies of a single molecule in the final and the initial states. When $E_f - E_i$ is negative, the negative value of the frequency corresponds to emission; when the frequency is positive, absorption of light is occurring. Although the changes in "internal" or potential energy of a molecule are quantized, the kinetic or "external" energy manifested by molecular translational motion is quantized in such small units that it appears unquantized, and the molecule may gain or lose translational energy in virtually any finite quantity.

Absorption spectra may be further classified into three types: rotation, rotation-vibration, and electronic. The third type includes rotational and vibrational interaction.

The *rotation* spectrum of a molecule is associated with changes which occur in the rotational states of the molecule without simultaneous changes