

YINGYONG BOPU XUE
(SHUANGYU)

高等学校教材

YINGYONG BOPU XUE(SHUANGYU)

应用波谱学

(双语)

韩小茜 主编

中国铁道出版社
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2008年·北京

内 容 简 介

本书被列入兰州交通大学“十五”教材资助计划,本书是针对高等学校化工专业编写的双语教材。全书共分四章,第一章是紫外可见光谱,第二章红外光谱,第三章核磁共振波谱,第四章质谱。

本教材可作为化学、化工等相关专业本科生的教材,也可供相关专业的研究生参考。

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出版说明

近年来,兰州交通大学认真贯彻落实教育部有关文件精神,不断推进教育教学改革。学校先后出资数百万元,设立了教学改革、专业建设、重点课程(群)建设、教材建设等项基金,并制定了相应的教学改革与建设立项计划、项目管理及奖励办法等措施。根据培养“基础扎实、知识面宽、能力强、素质高”的高级专门人才的总体要求,学校各院(部)认真组织广大教师积极参加教学改革与建设,开展系统的研究与实践,取得了一系列教学改革与建设成果。

通过几年来的深化改革,各学科专业制定了新的人才培养目标和规格,构建了新的人才培养模式和知识、能力、素质结构,不断修订完善专业教学计划和教学大纲。教学内容和课程体系的改革是教学改革的重点和难点,学校投入力量最大,花费时间最长,投入精力最多,取得的成效也最为显著。突出反映在教材建设方面,学校在各学科专业课程整合、优选教材的基础上,制定了“十五”教材建设规划,积极组织教材编写工作,通过专家论证和推荐,优化选题、优选编者,以保证教材编写质量,最后由学校教材编审委员会审定出版,确保出版教材教育思想的正确性、内容的科学性和先进性、形式的新颖性以及面向使用专业的针对性和适用性。近年来,通过广大教师的努力,相继编著了一批高水平、高质量,有特色的教材(包括文字教材和电子教材)。这些教材一般是由一些学术造诣较深、教学水平较高、教学经验比较丰富的教师担任主编,骨干教师参编,同行专家主审而定稿的。在教材中凝聚了编著教师多年的教学、科研成果和心血,这是他们在教学改革和建设中对高等教育事业做出的重要贡献。

本教材为学校“十五”教材建设资助计划项目,并通过了学校教材编审委员会审定。希望该教材在教学实践过程中,广泛听取使用意见和建议,适时进一步修改、完善和提高。

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前言 (Preface)

随着我国教育的不断深化,国际间的交流与合作日益频繁,对各种专业人才的需求不断提高,专业人才不仅要具有高水平的专业知识,还要具备高水平的外语交际能力。因此,国家教育部于2001年9月初下发通知,要求各高校使用英语等外语进行公共课和专业课的教学,力争三年内开出5%~10%的双语课,并为此引进了许多原版教材。在这种形势下,我校化工学院也逐渐开始实施双语课教学,开设了波谱分析等双语课程。在波谱分析课程的教学过程中,我们发现英文原版教材在教材的组织、内容和难度上与中文教材相比存在较大差异,为此,我们查阅了国内外相关教材和资料,尝试编著了这本波谱分析方面的双语教学用教材,为便于学生的学习,各章增加了与英文部分相对应的中文摘要和专业英语词汇的注释。

全书由韩小茜主编,共分四章,其中,第一章紫外可见光谱由赵丽编写,第二章红外光谱和第四章质谱由韩小茜编写,第三章核磁共振波谱由李丛芬编写。在本书编写过程中,韩相思提供了许多资料并参与了部分章节的写作。

本教材可作为化学、化工等相关专业本科生的教材,也可供相关专业的研究生参考。

本书承蒙兰州交通大学教务处的资助和兰州交通大学“青蓝”人才工程资助计划的资助得以出版,作者深表感谢。限于编者水平,书中错误和不当之处难免,恳请读者批评指正。

编 者

2006年12月于兰州交通大学

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Chapter 1 Ultraviolet and Visible Spectroscopy

1.1 Introduction

Spectroscopy is the measurement and interpretation of electromagnetic radiation absorbed, scattered, or emitted by atoms, molecules, or other chemical species. Most of what we know about the structure of atoms and molecules comes from studying their interaction with electromagnetic radiation, which is associated with the changes in the internal energy levels of the molecule. Different regions of the electromagnetic spectrum provide different kinds of information as a result of such interactions.

The electromagnetic spectrum ranges from very short wavelengths (including gamma and x-rays) to very long wavelengths (including microwaves and broadcast radio waves). We broadly refer to this radiation as light, even though only a very small portion of the spectrum is visible to the human eye. Figure 1.1 shows a brief overview.

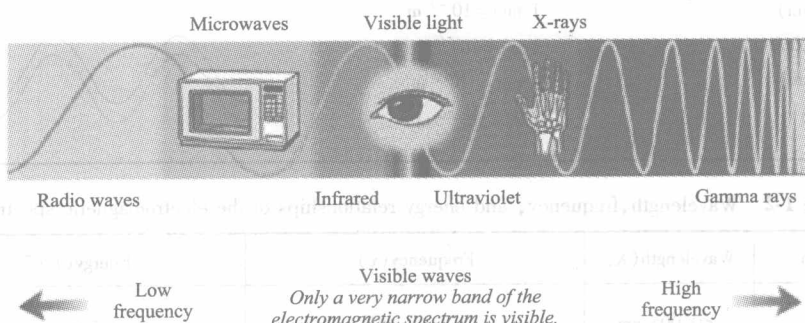


Figure 1.1 The electromagnetic spectrum

Electromagnetic radiation is propagated as a transverse wave. It consists of an oscillating electrical field and an oscillating magnetic field, perpendicular to each other. Electromagnetic radiation has wave-like properties as well as particle-like properties. Electromagnetic radiation possesses a certain amount of energy. The energy of a unit of radiation, called the photon. Electromagnetic radiation is characterized by its frequency or wavelength with the

energy of a photon. Quantitatively the relationship is as following equations 1.1 and 1.2. These equations tell us that frequency and energy change proportionally, but wavelength has an inverse relationship to these quantities. Table 1-1 gives some units commonly used to express wavelength. Table 1-2 summarizes the wavelength, frequency and energy relationships of the various parts of the electromagnetic spectrum.

$$\nu = c/\lambda \quad (1.1)$$

ν —frequency, λ —wavelength, c —velocity of light ($c = 3 \times 10^{10}$ cm/s)

$$E = h\nu \quad (1.2)$$

E —energy, ν —frequency, h —Plank's constant ($h = 6.6 \times 10^{-34}$ J · s)

Sometimes it is convenient to label the radiation with the inverse of the wavelength. An example is cm^{-1} . This inverse of centimeters is called the wave number, and the unit is used most often in infrared spectrometry. A measurement made in wave numbers is often denoted by $\bar{\nu}$. Then, the photon energy is the product of hc and the wave number. That is,

$$E = hc \bar{\nu} \quad (1.3)$$

Table 1-1 Common units used to express wavelength

Unit	Relation to Meter
Meter (m)	
Millimeter (mm)	1 mm = 10^{-3} m
Micrometer (μm)	1 μm = 10^{-6} m
Nanometer (nm)	1 nm = 10^{-9} m
Angstrom (\AA)	1 \AA = 10^{-10} m

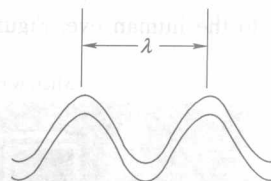


Table 1-2 Wavelength, frequency, and energy relationships of the electromagnetic spectrum

Spectrum	Wavelength (λ)	Frequency (ν)	Energy (E) *
γ -ray	< 0.005 nm	> 6.0×10^{19} Hz	> 2.5×10^5 eV
X-ray	0.005 ~ 10 nm	6.0×10^{19} ~ 3.0×10^{16} Hz	2.5×10^5 ~ 1.2×10^2 eV
ultraviolet	10 ~ 400 nm	3.0×10^{16} ~ 7.5×10^{14} Hz	1.2×10^2 ~ 3.1 eV
visible	400 ~ 800 nm	7.5×10^{14} ~ 3.8×10^{14} Hz	3.1 ~ 1.6 eV
infrared	0.8 ~ 1 000 μm	3.8×10^{14} ~ 3.0×10^{11} Hz	1.6 ~ 1.2×10^{-3} eV
microwave	1 ~ 300 mm	3.0×10^{11} ~ 1.0×10^9 Hz	1.2×10^{-3} ~ 4.1×10^{-6} eV
radiofrequency	> 300 mm	< 1.0×10^9 Hz	< 4.1×10^{-6} eV

* 1J = 6.241×10^{18} eV



When a substance is exposed to electromagnetic radiation, the substance can absorb the electromagnetic radiation only when the energy corresponds to some energy need or transition of a substance, taking it to a higher energy state, which is called transition (see Equation 1.4). Transitions in our substance can be: electronic transition (ΔE_e : 1 ~ 20 eV), vibrational transition (ΔE_v : 0.05 ~ 1 eV), rotational transition (ΔE_r : 0.005 ~ 0.050 eV). The last two are only seen for molecules.

$$\Delta E = h\nu \quad (1.4)$$

E —energy, ν —frequency, h —Plank's constant

X-ray (very high energy) is so energetic that they excite electrons past all the energy levels, causing ionization. Ultraviolet light (higher energy) has a shorter wavelength (approximately 10^{-7} m) than infrared radiation (lower energy), which has a wavelength of approximately 10^{-5} m. Energies in the ultraviolet-visible range excite electrons to higher energy levels within molecules. Infrared energies excite molecular vibrations, and microwave energies excite rotations. Radio-wave frequencies (very low energy) excite the nuclear spin transitions observed in NMR spectroscopy.

Example 1.1

Calculate the wavelength of a photon with an energy of 4.50×10^{-19} J.

Solution

$$E = \frac{hc}{\lambda}$$

$$\begin{aligned} \lambda &= \frac{hc}{E} = \frac{6.62 \times 10^{-34} \text{ J} \cdot \text{s} \times 3 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{4.50 \times 10^{-19} \text{ J}} \\ &= 4.41 \times 10^{-7} \text{ m} \\ &= 441 \text{ nm} \end{aligned}$$

Example 1.2

Calculate the energy in cm^{-1} of a photon with a wavelength of $4.00 \mu\text{m}$ (in the infrared region).

Solution

$$\begin{aligned} 4.00 \mu\text{m} &= 4.00 \times 10^{-4} \text{ cm} \\ \bar{\nu} &= \frac{1}{\lambda} = \frac{1}{4.00 \times 10^{-4}} = 2.50 \times 10^3 \text{ cm}^{-1} \end{aligned}$$

Example 1.3

Calculate the energy, in joule per mole of radiation, of a wave with wavelength $2.5 \mu\text{m}$. What type of radiant energy is this?

Solution

$$\begin{aligned} 2.5 \mu\text{m} &= 2.50 \times 10^{-6} \text{ m} \\ E &= \frac{hc}{\lambda} = \frac{6.6 \times 10^{-34} \text{ J} \cdot \text{s} \times 3 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{2.50 \times 10^{-6} \text{ m}} \end{aligned}$$

$$= 7.92 \times 10^{-20} \cdot \text{J}$$

$$E = 7.94 \times 10^{-20} \text{ J} \times 6.022 \times 10^{23} = 47.82 \text{ kJ}$$

1.2 The Principles of Ultraviolet and Visible Spectroscopy

1.2.1 Basics of Ultraviolet and Visible Light Absorption

The ultraviolet and visible (UV-Vis) spectroscopy involves the absorption of ultraviolet light by a molecule causing the promotion of an electron from a ground electronic state to an excited electronic state. The transitions are generally between a bonding or lone-pair orbital and an unfilled non-bonding or anti-bonding orbital. The wavelength of the absorption is then a measure of the separation of the energy levels of the orbitals concerned. Consequently, absorption spectroscopy carried out in this region is sometimes called “electronic spectroscopy”. A diagram showing the various kinds of electronic excitation that may occur in organic molecules is given in Figure 1.2. The highest energy separation is found when electrons in σ -bonds are excited, giving rise to absorption in the 120 ~ 200 nm range. This range, known as the vacuum ultraviolet, since air must be excluded from the instrument, is both difficult to measure and relatively uninformative. Only the two lowest energy ones ($\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$) are achieved by the energies available in the 200 ~ 800 nm spectrum. They involve excitation of electrons from p- and d-orbitals and π -orbitals, and, particularly, π -conjugated systems, which gives rise to readily measured and informative spectroscopy.

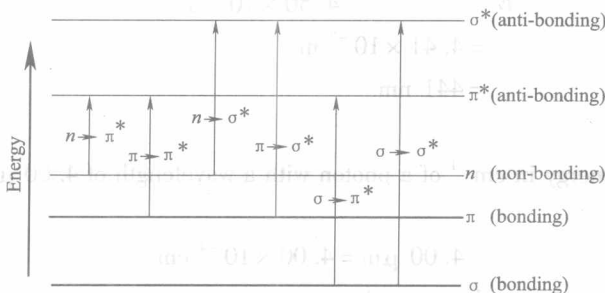


Figure 1.2 Relative energies of σ 、 π 、 π^* and σ^* orbital

1.2.2 The UV-Vis Spectrum and the Lambert-Beer Laws

The UV-Vis spectrum typically represents the absorption of light as a plot (Figure 1.3) of energy (as wavelength, λ , in nanometers, from $E = hc/\lambda$) versus the intensity of absorption (as absorbance, A , or molar extinction coefficient, ε , where ε is a rough measure of



the transition probability).

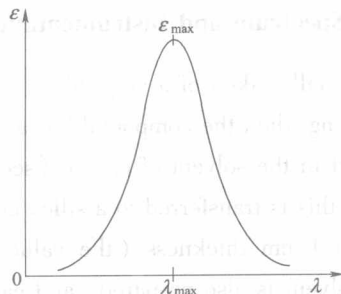


Figure 1.3 Typical UV-Vis Spectrum

UV-Vis spectra tend to show broad peaks and valleys. The absorption curves are broadened because vibrational and rotational levels are “superimposed” on top of the electronic levels. Peak broadening is illustrated in Figure 1.4.

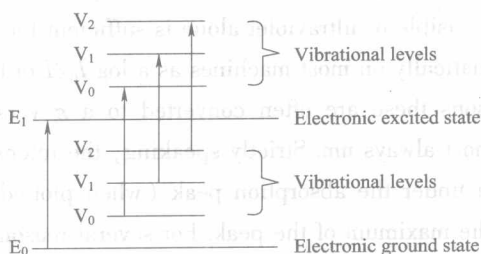


Figure 1.4 Peak broadening

When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. The absorbance, A , of the sample at a particular wavelength is governed by Lambert-Beer's law.

$$A = \log \frac{I_0}{I} = \log \frac{I_0}{I} = \epsilon \cdot b \cdot c \quad (1.5)$$

I_0 and I are the intensities of the incident and transmitted light respectively, b is the path length of the absorbing solution in centimeters, and c is the concentration in moles per liter, $\log I_0/I$ ($\log 1/T$) is called the absorbance or optical density; ϵ is known as the molar absorptivity and has units of $\text{cm}^{-1} \text{mol}^{-1} \text{L}$ but the units are, by convention, never expressed. It is a measure of how strongly the sample absorbs light at that wavelength. The spectral data that are most characteristic of a sample are as follows:

1. The wavelength(s) of maximum absorbance, called λ_{max} ;

2. The value of the molar absorptivity ε at each maximum, ε_{\max} .

1.2.3 Measurement of the Spectrum and Instrumentation

The UV-Vis spectrum is usually taken of a very dilute solution. An appropriate quantity of the compound (often about 1 mg when the compound has a molecular weight of 100 ~ 200) is weighed accurately, dissolved in the solvent of choice (see below), and made up to, for instance, 100 mL. A portion of this is transferred to a silica cell. The cell is so made that the beam of light passes through a 1 cm thickness (the value l in Eq. 1.5) of solution. A matched cell containing pure solvent is also prepared, and each cell is placed in the appropriate place in the spectrometer. This is so arranged that two equal beams of ultraviolet or visible light be passed, one through the solution of the sample, one through the pure solvent. The intensities of the transmitted beams are then compared over the whole wavelength range of the instrument. In most spectrometers there are two sources, one of 'white' ultraviolet and one of white visible light, which have to be changed when a complete scan is required. Usually either the visible or ultraviolet alone is sufficient for the purpose in hand. The spectrum is plotted automatically on most machines as a $\log I_0/I$ ordinate and λ abscissa. For publication and comparisons these are often converted to a ε versus λ or $\log \varepsilon$ versus λ plot. The unit of λ is almost always nm. Strictly speaking, the intensity of a transition is better measured by the area under the absorption peak (when plotted as ε versus frequency) than by the intensity of the maximum of the peak. For several reasons, most particularly convenience and the difficulty of dealing with overlapping bands, the latter procedure is adopted in everyday use. Since UV-Vis spectra are broad and lacking in detail, they are rarely printed as actual spectra. The spectral information is given as a list of the value or values of λ_{\max} together with the molar absorptivity for each value of λ_{\max} . The isoprene (2-methyl-1, 3-butadiene) spectrum is shown in Figure 1.5. It was obtained from a dilute hexane solution ($c = 4 \times 10^{-5}$ mol/L) in a 1 cm sample cuvette. A simple calculation using the above formula indicates a molar absorptivity of 20 000 at the maximum absorption wavelength.

Instruments for measuring the absorption of UV-Vis radiation are made up of the following components. Figure 1.6 shows a block diagram of a double-beam UV-Vis spectrophotometer.

1. Sources

Both deuterium and hydrogen lamps emit radiation in the range 160 ~ 375 nm. Quartz windows must be used in these lamps, and quartz cuvettes must be used, because glass absorbs radiation of wavelengths less than 350 nm. The tungsten filament lamp is commonly employed as a source of visible light. This type of lamp is used in the wavelength range of 350 ~ 2 500 nm. The energy emitted by a tungsten filament lamp is proportional to the fourth power



of the operating voltage. This means that for the energy output to be stable, the voltage to the lamp must be very stable indeed. Electronic voltage regulators or constant-voltage transformers are used to ensure this stability. Tungsten/halogen lamps contain a small amount of iodine in a quartz “envelope” which also contains the tungsten filament. The iodine reacts with gaseous tungsten, formed by sublimation, producing the volatile compound WI_2 . When molecules of WI_2 hit the filament they decompose, redepositing tungsten back on the filament. The lifetime of a tungsten/halogen lamp is approximately double that of an ordinary tungsten filament lamp. Tungsten/halogen lamps are very efficient, and their output extends well into the ultraviolet. They are used in many modern spectrophotometers.

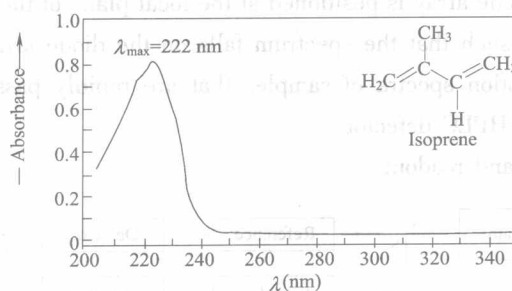


Figure 1.5 The UV spectrum of isoprene

2. Wavelength selector (monochromator)

All monochromators contain the following component parts: an entrance slit, a collimating lens, a dispersing device, a focusing lens (usually a prism or a grating) and an exit slit. Polychromatic radiation (radiation of more than one wavelength) enters the monochromator through the entrance slit. The beam is collimated, and then strikes the dispersing element at an angle. The beam is split into its component wavelengths by the grating or prism. By moving the dispersing element or the exit slit, radiation of only a particular wavelength leaves the monochromator through the exit slit.

3. Sample containers

The containers for the sample and reference solution must be transparent to the radiation which will pass through them. Quartz or fused silica cuvettes are required for spectroscopy in the UV-Vis region. These cells are also transparent in the visible region. Silicate glasses can be used for the manufacture of cuvettes for use between 350 nm and 2 000 nm.

4. Detector

The photomultiplier tube is a commonly used detector in UV-Vis spectroscopy. It consists of a photoemissive cathode (a cathode which emits electrons when struck by photons of radiation), several dynodes (which emit several electrons for each electron striking them)

and an anode. Photomultipliers are very sensitive to UV and visible radiation. They have fast response times. Intense light damages photomultipliers; they are limited to measuring low power radiation. The linear photodiode array is an example of a multichannel photon detector. These detectors are capable of measuring all elements of a beam of dispersed radiation simultaneously.

A linear photodiode array comprises many small silicon photodiodes formed on a single silicon chip. There can be from 64 to 4 096 sensor elements on a chip, the most common being 1 024 photodiodes. For each diode, there is also a storage capacitor and a switch. The individual diode-capacitor circuits can be sequentially scanned.

In use, the photodiode array is positioned at the focal plane of the monochromator (after the dispersing element) such that the spectrum falls on the diode array. They are useful for recording UV-Vis absorption spectra of samples that are rapidly passing through a sample flow cell, such as in an HPLC detector.

5. Signal processor and readout

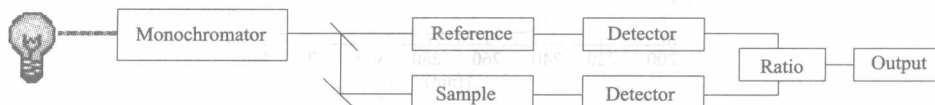


Figure 1.6 Block diagram of UV-Vis spectrometer

Example 1.4

A solution containing 1.00 mg ion (as the thiocyanate complex) in 100 mL was observed to transmit 70.0% of the incident light compared to an appropriate blank. (a) What is the absorbance of the solution at this wavelength? (b) What fraction of light would be transmitted by a solution of iron four times as concentrated?

Solution

(a) $T = 0.700$

$$A = \log \frac{1}{0.700} = \log 1.43 = 0.155$$

(b) $0.155 = ab(0.0100 \text{ g} \cdot \text{L}^{-1})$

$$ab = 15.5 \text{ L} \cdot \text{g}^{-1}$$

$$A = 15.5 \text{ L} \cdot \text{g}^{-1} (4 \times 0.0100 \text{ g} \cdot \text{L}^{-1}) = 0.620$$

$$\log \frac{1}{T} = 0.620$$

$$T = 0.240$$