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ФИЗИКО-ХИМИЧЕСКИЕ МЕТОДЫ ИССЛЕДОВАНИЯ В ОРГАНИЧЕСКОЙ И БИОЛОГИЧЕСКОЙ ХИМИИ

ИЗДАТЕЛЬСТВО «ПРОСВЕЩЕНИЕ» МОСКВА

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TO THE READER

Mir Publishers would be grateful for your comments on the content, translation and design of this book. We would also be pleased to receive any other suggestions you may wish to make.

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Preface

Current teaching courses in organic and biological chemistry make an extensive use of the results obtained by means of the physico-chemical laboratory techniques. The data on molecular structures in organic chemistry are derived from such physical techniques as UV, IR, NMR, EPR and mass spectrometries, refractometry and so on. This book deals with the main molecular spectroscopic techniques (UV, IR, Raman and NMR spectroscopies) and the dipole moments technique.

The laboratory techniques described here have been selected according to their use in organic chemistry for determining structures and physico-chemical properties of synthesis products, and according to the availability of the respective research instruments in the university laboratories. Hence, the major portion of the book is given to the UV and IR spectroscopy techniques. A brief discussion covers the fundamentals of a technique and its applications, then follow laboratory exercises and problems for students. The final section presents problems involving combined use of several physical and chemical laboratory techniques. The problems have been selected to take into account the teaching programme of the secondary school in order to make it useful for the school teachers, and students preparing for that career.

Chapter 1

Electron Absorption Spectroscopy

Similar to other molecular spectroscopic techniques, the electron absorption spectroscopy has a wide variety of applications in studies of the properties and structures of organic compounds, such as determination of structure and identification of a compound, evaluation of the purity of a product, analysis of kinetics and mechanisms of chemical reactions, quantitative determinations for simple and multicomponent systems, accurate measurements of the dissociation constants for acids and bases, analysis of the complexing processes (particularly those of the donor-acceptor nature), etc.

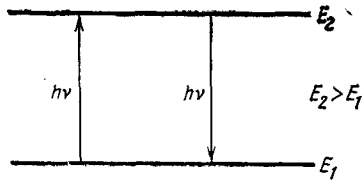
FUNDAMENTALS OF ELECTRON SPECTRA THEORY

Stationary States. Bohr's Postulates

The molecular spectroscopy (for the electronic, vibrational, rotational and other levels) studies the interactions between the electromagnetic radiation and the matter, and its theory stems from two concepts postulated by Bohr.

According to Bohr's postulates, atoms (or molecules) can exist without changing their energy, that is, without emission or absorption of radiation, only at certain stable states. The energies of these states comprise a discrete series $E_1, E_2, \ldots, E_x$ known as the system of energy lev-

Fig. 1.
Energy levels according to Bohr's postulates (the downward arrow denotes transition with emission, the upward arrow denotes transition with absorption).



els (Fig. 1). When an atom absorbs or emits some energy, ΔE, it jumps from one stable state to another one. The energy $h\nu$ of the absorbed or emitted quantum is equal to the variation ΔE of the system's energy. Hence, absorption or emission of radiation can occur only if the energy of the absorbed (emitted) quantum is equal to the difference between two energy levels:

$$\Delta E = E_2 - E_1 = h\nu = \frac{hc}{\lambda} \tag{1}$$

and

$$\nu = \frac{E_2 - E_1}{h} \tag{2}$$

Here c is the velocity of light, λ and ν are the wavelength and frequency of radiation, and h is Planck's constant.

Substitution of numerical values for h and c into eq. (1) yields

$$\Delta E \approx 120\,000 \frac{1}{\lambda} = 120\,000\bar{\nu}$$

Here ΔE is expressed in kilojoules per mole and λ in nanometers; $1/\lambda = \bar{\nu}$ (cm^{-1}) is the wave number and in spectroscopy it is often referred to as the frequency. There is a linear relationship between the wave number and the radiation energy: 1 cm^{-1} corresponds to 11.96 J/mole or $1.24 \cdot 10^{-4}$ eV.

Eq. (1) can yield directly the frequency ν of radiation.

Electromagnetic Radiation Energies and Types of Molecular Spectra

The molecular spectra have a considerably more complex structure than the atomic ones because in molecules, apart from the electronic degrees of freedom, there are also the rotational and vibrational degrees of freedom of the nuclei. The total energy E of a molecule can be expressed approximately (without taking into account the interaction between various types of motion) as a sum of the electronic, E_{el}, rotational, E_{rot}, and vibrational, E_{vib}, energies:

$$E = E_{el} + E_{vib} + E_{rot} \tag{3}$$

All the three types of molecular energy are quantized, that is, they can have only certain values proportional to Planck's constant, the intermediate energy values being forbidden. Theoretical and experimental results yield the following relationship between the above three types of energy:

$$E_{el} : E_{vib} : E_{rot} = 1 : \sqrt{\frac{m}{M}} : \frac{m}{M} \tag{4}$$

Here m is the mass of the electron and M is the mass of the nucleus. For instance, for the hydrogen molecule ($M \approx \approx 900\ m$), Eq. (4) yields

$$E_{el} : E_{vib} : E_{rot} = 1 : 1/30 : 1/900$$

The experimental results for the hydrogen molecule are: $E_{el} \approx 10$ eV, $E_{vib} \approx 0.5$ eV and $E_{rot} \approx 0.015$ eV, so that $E_{el} : E_{vib} : E_{rot} = 1 : 1/20 : 1/700$.

A considerable difference is thus apparent between the electronic, vibrational and rotational energies:

$$E_{el} \gg E_{vib} \gg E_{rot} \tag{5}$$

so that they correspond to different spectral ranges (Fig. 2).

When a molecule absorbs small amounts of energy (hundreds of joules per mole), it is excited to a higher rotational state while its vibrational and, of course, electron states remain unaltered. These energies correspond to absorption (emission) of the radiation with the wavelengths of 1-0.1 mm or more, that is, the wave numbers of 10-100 cm^{-1} or less. Thus, the purely rotational spectrum is found at the far infrared range or even at the radio-frequency (r.f.) range. At higher radiation energies the vibrational levels are excited; they correspond to the wavelengths of 2.5-100 μm, hence to wave numbers of 100-4000 cm^{-1}. Obviously, excitation of the vibrational levels entails excitation of the rotational levels, so that the resulting spectrum is a vibrational-rotational one. This spectrum is in the infrared range closer to the visible range. Excitation of the electronic levels occurs, typically, at much higher energies (of the order of hundreds of kilojoules per mole) corresponding to the visible and ultraviolet ranges of the spectrum (100-800 nm). At such radiation energies the vibrational and rotational spectra are also excited.

The electronic spectral range of Fig. 2 is shown in more detail in Fig. 3. The molecular electronic spectral range lies between $\sim 10^5$ cm^{-1} (100 nm) and $\sim 10^4$ cm^{-1} (1000 nm) and is classified into two ranges—the visible range between 400 and 1000 nm and the ultraviolet range between 400 and

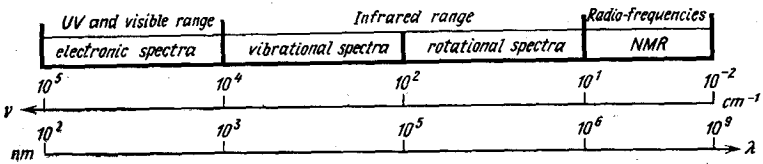


Fig. 2.
Radiation wavelengths and energy scale for rotational, vibrational and electron transitions.

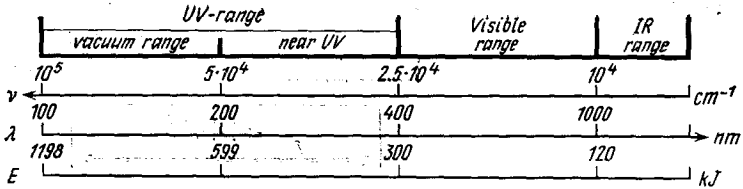


Fig. 3.
Radiation wavelengths and energy scale for electron transitions.

100 nm. This classification stems from a purely physiological fact that the human eye cannot see the ultraviolet light. In its turn, the ultraviolet range is divided into two subranges—the near subrange between 200 and 400 nm and the far, or vacuum, subrange between 100 and 200 nm. The latter is called the vacuum subrange because the air has the absorption bands in this subrange so that the spectral studies should be carried out in an evacuated spectrometer.

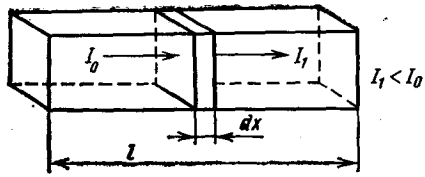
The Fundamental Law of Light Absorption (the Beer-Lambert-Bouguer Law)

The light absorption is the reduction of the light flux in a material, owing to conversion of the radiation energy into the internal energy of the material. The absorption of light should be distinguished from the scattering of light when the light flux along the initial direction is reduced owing to deflection of a fraction of the flux.

For the optical spectra (electronic, vibrational, rotational) there is a general radiation absorption law relating the absorbed radiation to the amount of the absorbing material.

Let us consider a thin layer of a material absorbing light (Fig. 4). The light flux I_0 incident on this layer is partially absorbed there so that the light flux leaving the layer is

Fig. 4.
Illustration to Beer's law.



$I_0 - dI$. Bouguer and Lambert have found that the light absorbed in the homogeneous material, dI, is proportional to the thickness, dx, of the absorbing layer. According to Beer's law, dI is proportional to the number of the absorbing particles in the layer dx, that is, to their concentration:

$$\frac{dI}{I} = -\varepsilon' \cdot c \cdot dx \tag{6}$$

Here c is the concentration of the absorbing particles (in moles per litre), and ε' is the probability of absorption by particles with unit concentration per unit incident flux. Integration of eq. (6) over x from 0 to l yields

$$\int_{I_0}^{I_1} \frac{dI}{I} = -\varepsilon' \cdot c \cdot \int_0^l dx \tag{7}$$

or

$$\ln \frac{I_1}{I_0} = -\varepsilon' \cdot c \cdot l \tag{8}$$

Introducing common logarithms, we obtain

$$-\log \frac{I_1}{I_0} = \varepsilon \cdot c \cdot l \quad (\varepsilon = 2.3 \cdot \varepsilon') \tag{9}$$

The parameter $-\log (I_1/I_0) = D$ is known as the optical density and the parameter $T = (I_1/I_0)\,100$ is known as the percent transmittance ($D = -\log T$). These parameters can be found experimentally.

Hence we obtain

$$D = \varepsilon \cdot c \cdot l \tag{10}$$

where ε is the molar extinction coefficient. Most spectrophotometric studies in chemistry make use of eq. (10) (deviations from eq. (10) and their causes are discussed below).

Energy Levels of Diatomic Molecules

The electron energy level of a molecule under normal conditions is known as the ground state (E_0), and the electronic levels with the higher energies are called the first, second and so on, excited states (E_1, E_2, . . .).

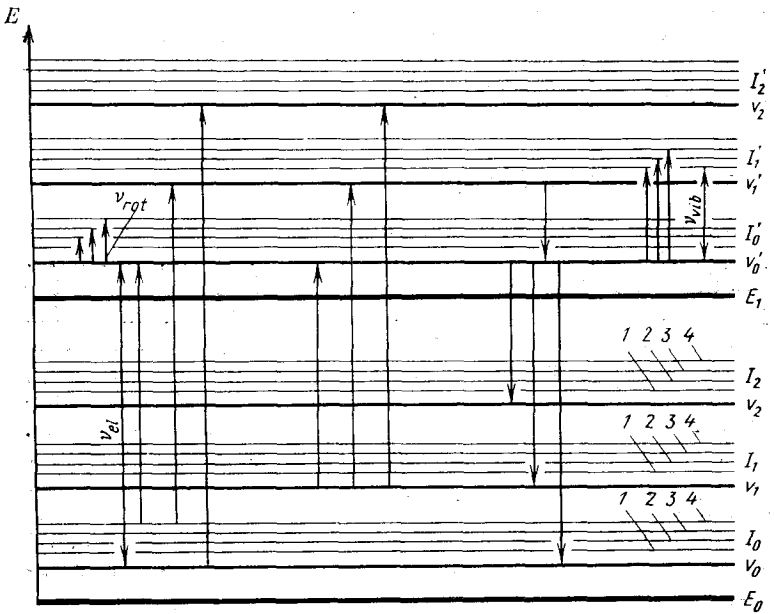


Fig. 5.
Electron, vibrational and rotational levels and transitions.

Each electronic state, E_0 for example, has its own system of vibrational levels consisting of one ground level (v_0) and several excited levels (v_1, v_2, . . .); in its turn, each vibrational state (for instance, v_1) has its own system of rotational levels consisting of one ground level (I_{11}) and several excited levels (I_{12}, I_{13}, I_{14}, . . .). Fig. 5 presents a schematic diagram of two electron levels (E_0 and E_1) of a molecule (actually, there are more than two levels), and the respective vibrational and rotational levels. It can be seen from the diagram that the lowest electron level to be occupied is the ground vibrational level v_0 rather than the purely electron level E_0. The explanation is that in the diatomic molecule (or a polyatomic molecule) there always occur some vibrations even at the absolute zero so that the electron cannot occupy the ground level E_0.

The Frank-Condon Principle

An excited state of a molecule differs significantly in the properties and structure from the ground state, which for the diatomic molecule implies a change in the shape of the potential function $E(r)$ (Fig. 6). For instance, excitation can lead to an increase or (more commonly) a decrease in the dissociation energy D, a decrease or (more commonly) an increase in the equilibrium distance, r, between the nuclei or, finally, the excited state can prove to be unstable.

The main problem encountered in analysis of a molecular electron spectrum can be formulated as follows. Assume that a radiation quantum $h\nu$ is absorbed by a molecule which is at the ground electron level and a vibrational level v. At what vibrational level will the molecule be found after absorption of a radiation quantum, or at which point of the potential curve can we find it with the highest probability? The answer is provided by the Frank-Condon principle which is based on the extremely fruitful idea that the electron