

POSSIBILITIES OF THE APPLICATION OF RAYLEIGH SPECTROSCOPY FOR THE
STUDY OF LIQUID HETEROCYCLIC COMPOUNDS (REVIEW)

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The investigation of the properties and structures of liquid systems by means of Rayleigh spectroscopy has undergone substantial development in the last 15-20 years [1-3]. This method makes it possible to determine the structure, conformations, and properties of molecules and the structure of liquid phases, including the structure of the least stable associates and complexes that decompose in 10^{-8} - 10^{-12} sec and are not detected by many other methods. One may study the kinetics and mechanisms of a number of ultrahigh-speed physicochemical processes that take place in liquid phases and, in many respects, determine the behavior of liquids; find the activity coefficients, heats of mixing, entropies of mixing, and diffusion coefficients of solutions; and measure the compressibility, thermal conductivity, heat capacity, temperature conductivity, and the rate of propagation of longitudinal and transverse sounds and their absorption coefficients. One may study processes involving migration of the energy of excitation in liquid phases and the details of the mechanism of elementary chemical acts. One may also investigate the peculiarities of the structure of a substance in the vicinity of the critical liquid-vapor point and the critical phase-separation point, and study the nature of phase transitions. Finally, one may obtain data on the molecular weights of polymers and oligomers, the conformational transformations of their molecules, the potential barriers to internal rotation, and the solvation of macromolecules.

There is no need here to prove that the chemistry of heterocyclic compounds, which include approximately half of the known natural substances and medicinal preparations, as well as a number of large-tonnage products of industrial chemical synthesis, requires not only profound studies of the reasons that determine the peculiarities of the properties and syntheses of these substances, but also convenient and simple methods for the monitoring of the quality of industrial products and measurements of the physicochemical properties of importance for chemical technology and technical applications. There is no universal method that makes it possible to obtain the answers to all of these problems. Here we will attempt to characterize the possibilities of Rayleigh spectroscopy.

The Rayleigh scattering in the spectrum of light scattered by a liquid is a very narrow symmetrical band (a "line"), the center of which corresponds to the frequency (ν_0) of the exciting light flux. The half-width ($\Delta\nu$) of the band does not exceed 10 cm^{-1} , i.e., $3 \cdot 10^{11}\text{ Hz}$. The integral intensity of this band follows the Rayleigh law $I \sim \nu_0^4$ if there are no macromolecules and dust in the liquid phase. Measurements of the Rayleigh scattering of the light reduce to finding the integral intensity (I) of the band mentioned above, the degree of depolarization (Δ) of the Rayleigh light scattering, and the spectrum of the Rayleigh line; i.e., the distribution of its intensity over the range of frequencies on the order of 10 cm^{-1} .

Integral Properties of Rayleigh Light Scattering Definitions. Suppose a stream of monochromatic parallel rays of unpolarized light is propagated along the X axis of the laboratory system of coordinates. Light passes through the liquid in a cuvette and is partially scattered. The frequency (ν_0) of the monochromatic emission corresponds to that range over which the liquid is transparent for this emission, i.e., the absorption bands due to intramolecular transitions are located far from ν_0 on the scale of frequencies. The electrical vectors of the incident and scattered radiation can be broken down into components that are

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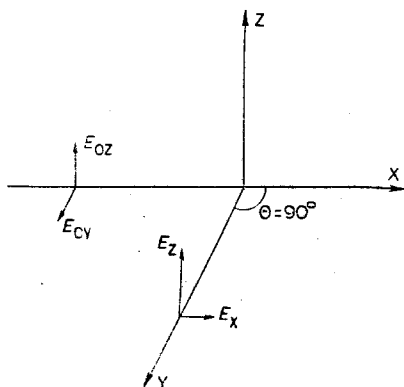


Fig. 1. Directions of the electrical vectors of the incident and scattered light for scattering at 90° .

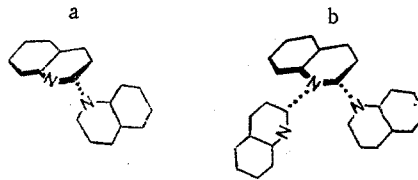


Fig. 2. Diagram of the structures of quinoline dimers (a, rotation about the C-H...N bond is almost free) and trimers (b, rotation about the C-H...N bonds is restricted).

linearly polarized along the axis of coordinates in the manner shown in Fig. 1. Angle θ between the directions of the incident and scattered radiation in Fig. 1 is 90° . A device for recording the scattered radiation is located at distance r from the center of the scattering volume (V) of the liquid. The intensity (I) of the scattered radiation and the degree of depolarization $\Delta = E_X^2/E_Z^2 = I_X/I_Z$ are measured. With the I_{90} and Δ_{90} values for $\theta = 90^\circ$ at one's disposal, it is easy to calculate I and Δ at any other scattering angle [1, 2]. The I value is usually only a small fraction (10^{-4} to 10^{-6}) of the intensity (I_0) of the incident radiation. When a number of precautions are observed, I can be measured with an accuracy of up to 1-5% [1, 2, 4].

The intensity of the scattered light (I_{90}) depends on I_0 , r , V, and the properties of the scattering medium:

$$I_{90} = I_0 \frac{V}{r^2} R_{90}, \quad (1)$$

where R_{90} is the absolute coefficient of light scattering or the Rayleigh coefficient. The R_{90} value at a given wavelength (λ_0) is determined by the properties of the scattering medium. The problem therefore reduces to finding R_{90} and the degree of depolarization of the scattered light (Δ_{90}). The R_{90} value is usually found by means of relative measurements by comparing the intensity (I_{90}) of the light scattered by any liquid with the intensity of the light scattered under the same conditions by a standard (benzene is most often used for this purpose). Then

$$R_{90} = \frac{I_{90}}{I_{90, C_6H_6}} R_{90, C_6H_6}, \quad (2)$$

The absolute coefficient of light scattering by benzene (R_{90} , C_6H_6) when $\lambda = 366$ nm at 25° is $106 \pm 5 \cdot 10^{-6} \text{ cm}^{-1}$, as compared with $46.4 \pm 0.5 \cdot 10^{-6} \text{ cm}^{-1}$ when $\lambda = 436$ nm at 20° , and $16.0 \pm 0.2 \cdot 10^{-6} \text{ cm}^{-1}$ when $\lambda = 546$ nm at 20° . The most nearly complete review of the results of measurements of R_{90} is presented in [2].

Fluctuations. If the molecules of a medium were distributed completely uniformly, i.e., if there were no fluctuations in the medium, the light scattered by the molecules owing to interference would be extinguished. Rayleigh light scattering is observed because fluctuations in the density ($\Delta\rho$), fluctuations in the concentration (Δx) (in solutions), and anisotropic fluctuations develop in the medium spontaneously in the course of thermal motion. Liquids are isotropic (liquid crystals are not considered here). The fluctuations in the density and concentration do not disrupt the isotropic character of a medium. Anisotropic fluctuations are random disruptions of the isotropic properties. The three forms of fluctuations mentioned above are statistically independent. The Rayleigh coefficient in the general case therefore consists of three independent parts — the coefficient of light scattering for density fluctuations (R_d), the coefficient of light scattering for concentration fluctuations (R_c), and the coefficient of light scattering for anisotropic fluctuations (R_a).

$$R_{90} = R_d + R_c + R_a. \quad (3)$$

The subscript 90 in the right-hand portion of Eq. (3) is omitted to simplify the symbols. The method for the calculation of R_d , R_c , and R_α from data on I and Δ has been described in [1, 2].

Isothermal Compressibility. From [2] it follows that

$$R_d = \frac{\pi^2}{2\lambda_0^4} (n^2 - 1)^2 \left(\frac{n^2 + 2}{3} \right)^2 kT \left(\beta_T - \frac{1}{\rho} \frac{V_h^2 - V_0^2}{V_h^2 V_0^2} \right). \quad (4)$$

Here, n is the refractive index of the liquid at light wavelength λ_0 , ρ is the density, k is the Boltzmann constant, T is the temperature in degrees Kelvin, V_0 is the rate of propagation of sound in the region of low sound frequencies, and V_h is the rate of propagation of sound with a wavelength of

$$\Lambda = n\lambda\sqrt{2}, \quad (5)$$

i.e., at frequencies of $\approx 10^{10}$ Hz (hypersonic frequencies). The V_h values are measured from data from the Rayleigh spectrum (see below). If there is internal rotation in molecules of heterocyclic derivatives and the liquid phases at 20° have a viscosity on the order of 10^{-2} p, the difference $V_h - V_0$ is small, and the second term in parentheses in Eq. (4) can be disregarded. The reasons for this are discussed in [5-9].

Equation (4) makes it possible to calculate the isothermal compressibility (β_T) of liquids from data on R_d with an accuracy on the order of 5-10%. This method for the determination of β_T is simpler and, in most cases, more accurate than others. For example, we have found that $\beta_T \cdot 10^{-12}$ cm²/dyn at 20° is 59 for pyridine, 41 for quinoline, 56 for 1,4-dioxane, 100 for trioxane, and 85 for tetrahydrofuran. Direct measurements at 20° , according to the data available in the literature, have been made only for pyridine and quinoline with an accuracy on the order of 10%. These measurements gave values of 67 and $45 \cdot 10^{-12}$ cm²/dyn, respectively. Within the limits of the experimental error, this is in agreement with the results of Rayleigh spectroscopy. We note that here we are dealing with the β_T value found for the interval of pressures (ΔP , on the order of 10 atm) that develop during average statistical fluctuations of the density in the volume elements whose linear dimensions do not exceed $\lambda/20$.

Associates and Complexes. One of the difficult problems in the chemistry of heterocycles is the determination of the composition, structure, and concentrations of the associates and complexes in liquid heterocycles and their solutions, as well as the types and energies of the chemical bonds that cause association or complexing. This is necessary for the study of mechanisms of chemical reactions and the comprehension and prediction of the properties of heterocyclic compounds. Rayleigh spectroscopy offers a number of methods for the solution of this problem. The most important of them is analysis of light scattered by anisotropic fluctuations.

In [2, 3, 10-12] it was shown that the anisotropic fluctuations in liquid phases are due to unstable associates and complexes, the average lifetime of which usually does not exceed 10^{-11} - 10^{-12} sec. A theory that makes it possible, from data on R_α , to determine the structure and concentration of such associates and complexes, as well as the enthalpies of their formation, has been evolved.

It is known that molecules are polarized under the influence of an electrical field — $\Delta \vec{\mu} = \alpha_{ij} \vec{E}$, where α_{ij} is the polarizability tensor of the molecules. One of the invariants of this tensor

$$\gamma_1^2 = \frac{1}{2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2] \quad (6)$$

is called the polarizability anisotropy of the molecule. Here we are dealing with a molecule of the monomer. The γ_1^2 value depends on the structure of the molecule and its symmetry. In the case of spherical symmetry, $\alpha_{xx} = \alpha_{yy} = \alpha_{zz}$, and $\gamma_1^2 = 0$. The polarizability anisotropy of molecules of associates or complexes of the p form (γ_p^2) is determined by the structure of these associates or complexes and by the principal values of the polarizability tensors α_{xx} , α_{yy} , and α_{zz} of those monomers of which the associates or complexes are composed. The formula linking R_α and the average statistical polarizability anisotropy of the molecules ($\langle \gamma_1^2 \rangle$) has the form

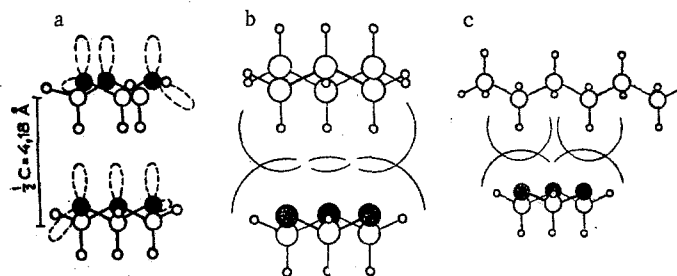


Fig. 3. Diagram of the structures of trioxane dimers (a), trioxane-cyclohexane complexes [14] (b), and trioxane-hexane complexes [14] (c).

$$R_a = \frac{104}{45} \left(\frac{\pi}{\lambda_0} \right)^4 \left(\frac{n^2 + 2}{3} \right)^4 \frac{N_A p}{M} \langle \gamma_1^2 \rangle. \quad (7)$$

Here N_A is Avogadro's number, and M is the relative molecular mass of the monomeric molecules. In the case of solutions, $M = \sum_i M_i x_i$, where x_i is the mole fraction of the i -th component.

The $\langle \gamma_1^2 \rangle$ value is calculated from data on R_a . The physically substantiated models of associates that satisfy the equation

$$\langle \gamma_1^2 \rangle = \sum_{p=1}^m \frac{N_p}{N} \gamma_p^2 \quad (8)$$

for one-component liquids or somewhat more complex equations for solutions are then selected. Here N_p is the number of associates of the p form in a unit volume, N is the total number of molecules of the liquid in a unit volume based on the monomer (i.e., as if there were no association), and γ_p^2 is the polarizability anisotropy of the associate of the p form ($p = 1, 2, \dots, m$). Methods for the calculation of γ_p^2 were examined in [2, 10-12]. If associates of several different structures are present in the liquid phase, instances in which the positive and negative terms in the

$\sum_{p=2}^m$ summation of Eq. (8) are such that the summation reverts

to zero and $\langle \gamma_1^2 \rangle = \gamma_1^2$ are possible. In this case the liquid behaves, with respect to light scattering by anisotropic fluctuations, as if it were unassociated, i.e., any mutual orientations of the molecules would be equally probable. Rayleigh light scattering by anisotropic fluctuations "does not detect" directly the presence of such n -dimensional associates of the p form, the structure of which leads to the relationship $\gamma_p^2 = n\gamma_1^2$. The contribution of n -dimensional associates of this sort to R_a does not differ from the contribution of n unassociated molecules.

The structure of the associates should be such that not only the $\langle \gamma_1^2 \rangle$ values and their changes with temperature, but also the behavior of the $\langle \gamma_1^2 \rangle$ values of solutions and the results of studies of a liquid by acoustic spectroscopy, dielectric radiospectroscopy, NMR, IR, and Raman spectroscopy, and thermodynamic methods, etc., are consistently explained.

The dimers and trimers formed by means of C-H...N hydrogen bonds play the principal role in pyridine and quinoline. The enthalpy of these bonds is about 2 kcal/mole. The structures of quinoline dimers are depicted in Fig. 2. The molecules of aromatic heterocycles, like benzene molecules [12], can also form weaker bonds in which the C-H groups of one molecule and the π orbitals of another molecule participate. The C-H groups may participate in bonds with the π orbitals of unsaturated hydrocarbons. The enthalpy of bonds of this type is about 1 kcal/mole. Complexes due to bonds between the nitrogen atom of pyridine and the C-H group of chloroform and between the C-H group of chloroform and the π orbitals of pyridine are detected in pyridine-chloroform solutions. The average enthalpy of one such bond is 2.5 ± 0.5 kcal/mole [13]. Trioxane molecules form associates through C-H...O bonds [14]. The enthalpy of these bonds is $\approx 1.4 \pm 0.5$ kcal/mole. Two trioxane molecules may interact with one another to form three such bonds, as depicted in Fig. 3. The polymeric trioxane associates remind one of a "bookcase." Weak C-H...O bonds undoubtedly exist in liquid dioxane. The weak H bonds of the CH₂ and CH₃ groups can be detected when their effect on the structure of the liquid phase is not masked by the action of the stronger O-H...O, N-H...N, and other bonds.

The association of heterocyclic and other molecules is conveniently studied in those binary solutions in which the principal values of the polarizability tensor (α_{XX} , α_{YY} , and α_{ZZ}) are small for the second component (water, methanol, etc.).

For the calculation of the γ_p^2 values of associates of the p form consisting of axially symmetrical molecules it is sufficient to know the γ_1^2 values. In other cases, data regarding all three principal values of the polarizability tensor of the monomers that form the associate or complex are required. The method gives additional independent information regarding the associates and complexes detected by other methods. It opens up a possibility for the investigation of those associates that cannot in principle be studied by means of dielectrical, IR, and Raman measurements. It also makes it possible to study the association of heterocycles dissolved in water, methanol, and a number of other solvents not only at low concentrations but also at high concentrations of the dissolved heterocyclic compounds.

Polarizability Anisotropy of Monomers and Principal Values of the Polarizability Tensor. These quantities are needed for the determination of the structure of polar or nonpolar molecules and for the analysis of the Raman spectra and the behavior of the molecules in electric fields. The measurements can be made in rarefied vapors and solutions from data on light scattering by anisotropic fluctuations. For vapors in a number of cases the measurements are complicated by the effect of the Raman spectrum of the rotational transitions [15] and the Raman spectrum of the low-frequency vibrational transitions of the associates. For solutions both of these factors are unimportant, whereas the associates and complexes may affect the R_α value. In the case of vapors, the values are calculated from the formula

$$\gamma_1^2 = \frac{45\Delta_{90}\alpha^2}{6-7\Delta_{90}}, \quad (9)$$

which takes into account the contribution of the rotational Raman spectrum (see [15]). Here α is the average polarizability of the vapor molecules [$\alpha = (\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ})/3$], calculated on the basis of the refractive indices in the vapors from the Lorenz-Lorentz equation. In the case of solutions, one analyzes the $\langle\gamma_1^2\rangle = f(x)$ function, where x is the mole fraction of the substance under investigation. It is convenient to use methanol, water, and other liquids whose molecules differ with respect to the smallness of α_{XX} , α_{YY} , and α_{ZZ} as the solvent. The method was developed in [2, 10]. With the existing accuracy in the measurements of R_{90} and Δ , the concentration range $x < 0.02$ is, as a rule, not yet accessible for study. For molecules that have axial symmetry two of the three principal values of the polarizability tensor are identical. They can be found from data on γ_1^2 and α . In the remaining cases data on the Kerr constant or studies of the polarizability anisotropy of the complexes are required [2]. For example, when $\lambda = 488$ nm, $\gamma_1^2 \cdot 10^{48}$ cm⁶ of quinoline molecules in vapors is 189.* In dilute solutions in methanol when $\lambda = 436$ nm, $\gamma_1^2 \cdot 10^{48}$ cm⁶ is 164 ± 25 , as compared with 138 ± 14 when $\lambda = 546$ nm. In pyridine vapors* when $\lambda = 488$ nm, $\gamma_1^2 \cdot 10^{48}$ cm⁶ is 28.6. For dioxane dissolved in methanol when $\lambda = 546$ nm, $\gamma_1^2 \approx 1.0 \cdot 10^{-24}$ cm⁶. In the case of quinoline molecules when $\lambda = 546$ nm, $\alpha_{XX} = 18 \cdot 10^{-24}$ cm³, $\alpha_{YY} = 23 \cdot 10^{-24}$ cm³, and $\alpha_{ZZ} = 9.6 \cdot 10^{-24}$ cm³.

Dispersion of $\langle\gamma_1^2\rangle$ and γ_1^2 . If the molecules have absorption bands at 3000-4000 Å, as in the case of quinoline, in the optical range of wavelengths the polarizability tensor, within the limits of experimental error, is symmetrical, but dispersion of γ_1^2 and $\langle\gamma_1^2\rangle$ is observed. A detailed analysis of this problem has shown that the dispersion of γ_1^2 and $\langle\gamma_1^2\rangle$ in the cases studied by us is similar to the dispersion of refractive index n , and the main values of the polarizability ellipsoid vary with the wavelength in proportion to the average polarizability. Equation (4) for R_d and Eq. (7) for R_α in these cases remain valid, as confirmed, in particular, by the absence of a dependence of β_T on λ . The question of the laws of the scattering of light whose frequency corresponds to the absorption band as yet remains an open one.

*The measurements of the γ_1^2 values of molecules in vapors were made by F. I. Panachev, E. Yu. Korableva, and M. I. Shakhparonov. Inasmuch as data on the α values of pyridine and quinoline molecules in vapors are not available, the γ_1^2 values were calculated by means of the α values found from data on the refractive indices and the densities of the liquid phases; this possibly (as for benzene) gives somewhat elevated values. The degree of accuracy of the γ_1^2 values for measurements in vapors is therefore not estimated. The γ_1^2 and α values of molecules in vapors and in the liquid phase may differ.

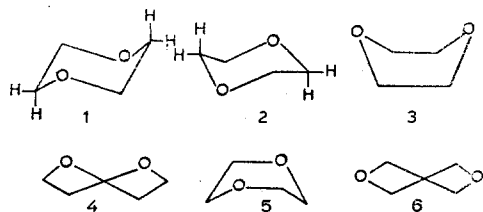


Fig. 4. Conformations of 1,4-dioxane molecules.

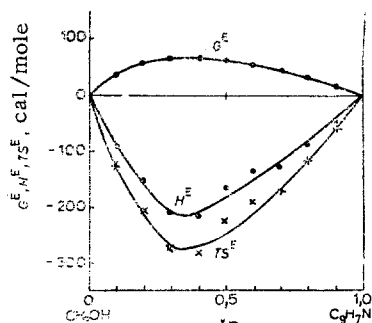


Fig. 5. Excess thermodynamic functions — free enthalpy (G^E), enthalpy (H^E), and TSE (S^E is the excess enthalpy) of quinoline-methanol solutions at 20°C.

Conformational Transformations. If the association and complexing in the liquid phase do not affect the $\langle \gamma_i^2 \rangle$ value and the monomer molecules are capable of conformational transformations accompanied by changes in their polarizability anisotropy, studies of the R_q value make it possible to investigate these transformations [2]. In this case, we have

$$\gamma_1^2 = \sum_i c_i \gamma_i^2, \quad (10)$$

where γ_i^2 is the polarizability anisotropy of the i -th conformer, and c_i is its mole fraction. Thus, for example, 1,4-dioxane molecules have the six conformations depicted in Fig. 4. Conformations 3 and 4 are polar, whereas conformations 1, 2, 5, and 6 are nonpolar. The polarizability anisotropies of the first five conformations are identical. The polarizability anisotropy of the sixth conformation (the twist form) is greater than the anisotropies of the preceding conformations. In dioxane, associates due to C-H...O bonds can, with equal probability, have many different forms, so that the mutual orientation of adjacent molecules is close, on the average, to chaotic. When dioxane is heated from 20 to 90°, the γ_1^2 value increases by ~40%; this can be explained by an increase in the concentration of the twist form. In dilute aqueous solutions, the stability of the polar conformations of dioxane increases due to the energy (E_R) of reactive interaction of their dipoles with the surrounding medium, and $E_R \approx 1.3$ kcal/mole. This should lead to a decrease in the concentration of the nonpolar twist form and, consequently, to a decrease in the γ_1^2 value. An analysis of the results of measurements of light scattering by dioxane-water solutions [16] confirms this conclusion. Thus, Rayleigh spectroscopy makes it possible to study both polar and nonpolar conformations of molecules.

Activity Coefficients and Excess Thermodynamic Functions of Solutions. The theory evolved in [17] leads to an expression linking the coefficient of light scattering by concentration fluctuations (R_C) of a two-component nonideal solution with the derivative of the activity coefficient (f_1) with respect to the mole fraction (x_1) of component 1.

$$R_C = \frac{2\pi^2}{\lambda_0^4} \frac{V_M x_1 n^2 \left(\frac{\partial n}{\partial x_2} \right)_{PT}^2}{(N_A/x_2) + (N_A f_1/x_1) (\partial f_1/\partial x_1)_{PT}}. \quad (11)$$

Here V_M is the molar volume. The remaining symbols are the same as those given earlier. For an ideal solution, where $f_1 = 1$ when $0 \leq x_1 \leq 1$, we have

$$R_{C,id} = \frac{2\pi^2}{\lambda_0^4} \frac{V_M x_1 x_2}{N_A} n^2 \left(\frac{\partial n}{\partial x_2} \right)_{PT}^2. \quad (12)$$

From Eqs. (11) and (12) and the Gibbs-Duhem relationship it follows that

$$1 - \frac{R_{C,id}}{R_C} = - \left(\frac{\partial \ln f_1}{\partial \ln x_1} \right)_{PT} = - \left(\frac{\partial \ln f_2}{\partial \ln x_2} \right)_{PT}. \quad (13)$$

The activity coefficients are obtained by integration

$$\ln f_i = \int_0^{x_i} \frac{1}{x_i} \left\{ 1 - \frac{R_{c, id}}{R_c} \right\} dx_i \quad (i=1, 2). \quad (14)$$

Knowing $\ln f_i$ ($i = 1, 2$) one calculates the excess free enthalpy of mixing (G^E) of components 1 and 2, the enthalpy of mixing ($H^E = H^M$), and the entropy of mixing (S^E) by means of known thermodynamic relationships (for example, see [18]). For solutions with positive deviations from ideality and a nonzero $(\partial n / \partial x_2)_{PT}$ derivative, this method for the determination of the indicated thermodynamic properties is simple and convenient, and, in a number of cases [19], it is inferior in accuracy only to the results of vapor pressure measurements if they are made by the most precise methods. The excess thermodynamic functions of quinoline-methanol solutions at 20° calculated from data on R_c are presented in Fig. 5.

Rayleigh Light Scattering Spectra. Let us now assume that a monochromatic ray of light, the wavelength of which is λ_0 , is linearly polarized in such a way that the electrical vector vibrates along the Z axis ($E_{0Z} \neq 0$, $E_{0Y} = 0$) or along the Y axis ($E_{0Y} \neq 0$, $E_{0Z} = 0$) (see Fig. 1). The ray impinges on a cuvette filled with an isotropic liquid in a thermostat. The scattering volume of the liquid is V. Let us examine the spectrum of the Z or X component of the radiation scattered by the liquid at right angles ($\theta = 90^\circ$).

Let us assume that the electrical vector of the impinging ray is directed along the Z axis and that that portion of the scattered radiation whose electrical vector is also directed along the Z axis, i.e., the I_{ZZ} component of the scattered light, is under investigation. Here and subsequently, the first subscript in I_{ij} denotes the direction of the electrical vector of the incident radiation, while the second subscript denotes the coordinate axis along which the electrical vector of the scattered radiation vibrates.

The I_{ZZ} component of the scattered radiation is made up of the "isotropic" scattering of light by fluctuations in the density and concentration (its degree of depolarization is zero) and of light $I_{a, ZZ}$ scattered by anisotropic fluctuations. In the case of linearly polarized incident radiation the degree of depolarization of the "nonisotropic" scattering is $\Delta_a = I_{aZX} / I_{aZZ} = 3/4$. If the spectrum of the $I_{aZZ} = I_{ZX}$ component is measured and multiplied by $4/3$, and the result is subtracted from the spectrum of the I_{ZZ} component, the remaining portion of the I_{ZZ} component is due to density fluctuations and, when the scattering phase is a solution, also concentration fluctuations.

Mandelstamm-Brillouin Light Scattering Spectrum. We will initially examine only that portion of the isotropic scattered radiation that is due to density fluctuations ($\Delta\rho$), i.e., $I_{d, ZZ}$. The $I_{d, ZZ}$ spectrum consists of three lines (the "Rayleigh triplet"). The Rayleigh triplet of the $I_{d, ZZ}$ component of light scattered by pyridine is presented in Fig. 6 [5]. By changing scattering angle θ , one can study the rate of propagation of sound at various frequencies. By determining the half-width of the Mandelstamm-Brillouin component one can find the coefficient of sound absorption (α_{ac}) at frequency $\Delta\nu$. At present, this method makes it possible to measure the speed of sound and the coefficient of sound absorption in liquids at frequencies of sound vibration from 3 to 10 GHz (at $\approx 180^\circ$) that are inaccessible to measurement by other methods [4]. The possibility of extending studies of the acoustic properties of liquid phases by this method to the range of low sound frequencies was examined in [20]. Dispersion (i.e., a dependence on the frequency of the sound vibrations) of the hypersonic speed in pyridine, thiophene, and furan was detected in [6, 21, 22]. It was shown that this process is due to conversion of the energy of alternating motion of the molecules to the energy of intramolecular vibrations during thermal motion. Subsequent experimental and theoretical investigations of the migration of the energy of the vibrational excitations of these and other molecules were made in [7, 8], where it was found possible to establish the fundamental principles of this phenomenon. Acoustic dispersion may be due to those processes (reactions) that are accompanied by a change in the volume of the system and a heat effect (or at least by one of these phenomena). Many reactions involving association and complexing, conformational transformations, and processes involving the formation and disintegration of concentration fluctuations fall under this heading. If these processes are ultrahigh-speed processes, i.e., if they take place with characteristic times on the order of 10^{-6} - 10^{-12} sec, studies of the Mandelstamm-Brillouin spectrum are useful for the establishment of their kinetics and mechanisms [3].

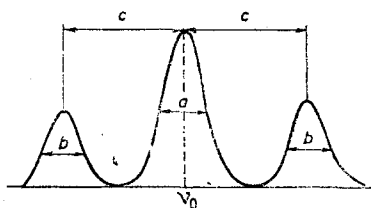


Fig. 6

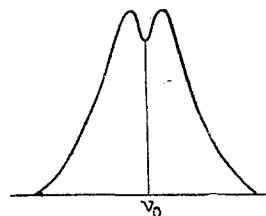


Fig. 7

Fig. 6. Spectrum of the "Rayleigh triplet" in pyridine at 25°C. Gross components and Mandelstamm-Brillouin components: a) width of the Gross component; b) width of the Mandelstamm-Brillouin components; c) shift of the Mandelstamm-Brillouin components relative to the frequency of the incident light ($\Delta\nu = 0.244 \text{ cm}^{-1}$).

Fig. 7. Spectrum of the IZX, α component of light scattered by quinoline at 20° (Leontovich-Fabelinskii doublet components).

Spectrum of the Central Component of the Rayleigh Triplet (the Gross Component*). In individual liquids (see Fig. 6) the Gross component is due to isobaric fluctuations in the density that are proportional to the fluctuations in the entropy. In contrast to adiabatic density fluctuations, isobaric density fluctuations do not migrate with time. The maximum of the Gross component therefore corresponds to the frequency (ν_0) of the exciting radiation. The average lifetime of the isobaric density fluctuations (τ) is determined by the coefficient of temperature conductivity (χ):

$$\tau \approx \frac{1}{\chi} = \frac{\rho C_P}{\kappa}. \quad (15)$$

Here C_P is the heat capacity at constant pressure, and κ is the coefficient of thermal conductivity. By studying the spectrum of the Gross component, one can determine the coefficient of temperature conductivity [23] and, if C_P is known, the coefficient of thermal conductivity (κ). The accuracy of these measurements increased markedly with the development of gas lasers. The contour of the Gross component is determined by the Lorentz function. The half-width of the line ($\Delta\nu_d$) when $\theta = 90^\circ$ is

$$\Delta\omega_d = 8\pi^2 n \chi / \Lambda_d^2, \quad (16)$$

where Λ_d is the wavelength of the Fourier component of the isobaric density fluctuations that is observed in the scattered radiation.†

The ratio of the integral intensity of the Gross component to the integral intensity of the two Mandelstamm-Brillouin components (2IMB) is, according to L. D. Landau and G. Placzek (1933),

$$I_G / 2I_{MB} = \frac{\beta_T - \beta_S}{\beta_S} = \frac{C_P}{C_V} - 1. \quad (17)$$

Here β_S is the adiabatic compressibility, and C_V is the heat capacity at constant volume. M. S. Tunin has shown (1962) that in those cases in which dispersion of the speed of sound is observed for acoustical frequencies up to 10^{10} Hz (the speed of sound increases with frequency, and β_S , β_T , C_P , and C_V decrease correspondingly), one must take into account the effect of the acoustic dispersion on the frequency ($\Delta\omega$).

Investigations of the spectrum of the Gross component in solutions make it possible to find diffusion coefficient D . The formula for the calculation of D has the form

$$\Delta\omega_c = 8\pi^2 D / \Lambda_c^2, \quad (18)$$

where $\Delta\omega_c$ is the half-width of the Lorentz line due to light scattering by concentration fluctuations (Δx), and Λ_c is the length of the concentration wave observed in the scattered radiation [24-27]. A method for the measurement of $\Delta\omega_d$ and $\Delta\omega_c$ is described in [27]. Despite

*Detected by E. F. Gross in 1930.

†Here and subsequently, ω is the rotational frequency ($\omega = 2\pi\nu$).

the extremely small widths of these lines, investigational difficulties have been overcome in recent years. The existing methods and apparatus, together with the output of data from computers, make it possible to obtain all the necessary information in a few minutes.

Spectrum of Light Scattered by Anisotropic Fluctuations. Suppose the electrical vector of a linearly polarized monochromatic light ray vibrates along the Y axis. Scattering angle θ is 90° . Let us consider the spectrum of the $I_{YX,\alpha}$ component of the scattered radiation

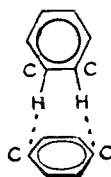
$$I_{YX,\alpha} \sim \langle (\Delta\epsilon_{YX})^2 \rangle V^* \quad (19)$$

Here $\Delta\epsilon_{YX}$ is the anisotropic component of the dielectric permeability of the optical range of frequencies in a volume element of the liquid equal to V^* .

As we have already stated above, the spectrum of light scattered by anisotropic fluctuations depends on the kinetics and mechanism of the processes involved in the formation and disappearance of these fluctuations, i.e., unstable associates or complexes formed during thermal motion. A theory that makes it possible to link the $I_{YX,\alpha}(\omega)$ spectrum with the values that characterize the kinetics and mechanism of the ultrahigh-speed reactions of association and complexing mentioned above was developed in [28, 29]. Methods for the calculation of reactions involving association in liquid phases were developed in [9] (see also [2]). This method is convenient for the study of ultrahigh-speed reactions that occur in liquid phases with characteristic times on the order of 10^{-10} - 10^{-12} sec. Thus, for example, measurements of the spectrum of light scattered by anisotropic fluctuations in dioxane at 20 to 100° were made in [30]. The distribution of the intensity in the spectrum is the sum of two Lorentz functions of the form $A/(1 + \omega^2\tau^2)$. At 20° , relaxation time $\tau_1 = 1.1 \cdot 10^{-11}$ sec, and $\tau_2 = 0.5 \cdot 10^{-12}$ sec. The spectrum of light scattering by anisotropic fluctuations in dioxane-chloroform and thiophene-chloroform solutions changes substantially because of the formation of unstable dioxane-chloroform and thiophene-chloroform complexes and chloroform associates at high chloroform concentrations [31].

Leontovich-Fabelinskii Effect. Elastic stresses and deformations appear during the development of anisotropic fluctuations in some relatively viscous liquids. This leads to propagation in the liquid phase of rapidly attenuating transverse vibrations. The liquid particles vibrate in a plane perpendicular to the direction of propagation of the deformations indicated above. In 1941, M. A. Leontovich [32] showed that this process should lead to splitting of the $I_{ZX,\alpha}$ component of Rayleigh light scattered by anisotropic fluctuations. The splitting of the $I_{ZX,\alpha}$ spectrum of light scattered in quinoline and some other liquids was first observed by Fabelinskii and his co-workers [33] (see Fig. 7). This phenomenon has been called the Leontovich-Fabelinskii effect [34]. The distance between the Leontovich-Fabelinskii components ($\Delta\nu_{LF}$) on the frequency scale is considerably shorter than for the Mandelstamm-Brillouin components. For quinoline at 20° according to [35], $\Delta\nu_{LF} = 4 \cdot 10^{-2} \text{ cm}^{-1} = 1.2 \cdot 10^9 \text{ Hz}$, and $V_\perp = 3 \cdot 10^4 \text{ cm/sec}$; whereas the rate of longitudinal hypersonic waves (V_h) is $1572 \pm 30 \cdot 10^5 \text{ cm/sec}$ at 70° . An investigation of the properties of transverse sound seems of great interest for the establishment of the mechanism and kinetics of fast collective processes that occur in liquid phases.

Here we have spoken of applications of Rayleigh light scattering in the investigation of low-molecular-weight liquid heterocyclic compounds, having in view compounds such as these within the usual understanding of this term. If molecules and associates that contain rings consisting of various atoms joined not only by strong chemical bonds but also by weak bonds are considered, the number of heterocycles studied by the methods of Rayleigh spectroscopy sharply increases, and the distinction between heterocyclic and other compounds then vanishes. Cyclic dimers of carboxylic acids, which were investigated in [36, 37], or associates of benzene with rings of the form



which were investigated in [12, 38], are examples of such heterocycles.

We have restricted ourselves here to a description of the properties and applications of strictly Rayleigh scattering of light whose intensity is subject to the Rayleigh law $I \sim \nu^4$. The Rayleigh law is violated in the vicinity of the critical phase-separation points of solutions, the critical liquid-vapor point, and in polymer solutions.

A study of light scattering in the vicinity of the phase-separation point gives rich and comprehensive information regarding the structure of a substance in the vicinity of this critical point and regarding the kinetics of processes involved in the formation and breakdown of fluctuations. Reviews of these investigations are available in [24-26, 39-41]. Light scattering in solutions of polymers is one of the principal methods for the investigation of these systems (for example, see [42]). The great possibilities of this method for the investigation of polymers whose links are heterocycles can be thoroughly illustrated in the case of cellulose and its derivatives [43].

Thus Rayleigh spectroscopy makes it possible to study the structure of liquid heterocycles and determine many physicochemical properties of these and other liquids of importance for chemistry and technology. Advantages of the method include the possibility of obtaining comprehensive and, in a number of cases, unique information. A disadvantage is the present lack of standard apparatus by means of which one might be able to make measurements at a level corresponding to that of laboratory devices. This difficulty is due to the novelty of the method. The creation of standard measuring devices based on the best of the available experimental equipment is fully possible.

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SYNTHESIS OF γ -BUTYROLACTONES FROM AMIDO DERIVATIVES OF AROMATIC KETONES

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Derivatives of γ -butyrolactones were synthesized by bromination of N,N¹-disubstituted (1-phenyl-2-benzoyl)ethylmalonic acid amides.

It is known that spiroketolactones [1, 2] are formed by bromination of amido derivatives of indanediones and tetralones. In the present research we have studied the possibility of the preparation of γ -butyrolactones from amido derivatives of noncyclic aromatic ketones. Inasmuch as the γ -butyrolactone ring is present in a number of natural antibiotics and alkaloids [3, 4], its formation seems of interest for the synthesis of potential physiologically active compounds.

(1-Phenyl-2-benzoyl)ethylmalonic acid N,N¹-dialkylamides (Ia-c) [5] were used as the starting compounds. α -(N-Alkylcarbamoyl)- β -phenyl- γ -benzoyl- γ -butyrolactones IVa-c were isolated in the bromination of diamides Ia-c with bromine in acetic acid.

Like the IR spectra of starting amides I, the spectra of lactones IV contain the absorption of a ketone carbonyl group at 1685-1699 cm⁻¹ and of an amide carbonyl group at 1665-1670 cm⁻¹. In contrast to the spectra of starting amides I, an intense maximum at 1778-1790 cm⁻¹,

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