The number of photodissociated $^{15}NH_3$ molecules is determined mainly by the intensity of the UV source and by the irradiation time. In our experiments, we dissociated several per cent of the ammonia molecules. The retention of the selectivity in the secondary chemical reaction serves as an additional confirmation that the photodissociation of ammonia follows the scheme proposed in [4].

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SPECTRUM OF DEPOLARIZED LIGHT SCATTERED IN A SOLUTION NEAR THE CRITICAL LAMINATION POINT

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The spectrum of polarized light scattered as a result of fluctuations of the entropy, pressure, and concentration, turned out to be a sensitive tool for the investigation of the most subtle processes that occur near the critical points of a pure substance and of a solution that becomes laminated (cf., e.g., [1 - 3]). There is every reason for assuming that the spectrum of light scattered as a result of anisotropy fluctuations - the Rayleigh line wing [4 - 6] - will also experience significant changes near the critical points of a pure substance or a solution.

We report here the results of the first investigation of the temperature kinetics of the Rayleigh line wing near the critical lamination point of the solution. The spectrum of the Rayleigh line wing turned out to be extremely sensitive to temperature variation when the critical point was approached, and revealed interesting singularities that were difficult to predict. We investigated solutions of nitrobenzene in n-hexane (mixture of 50% nitrobenzene by weight in n-hexane, critical lamination temperature t_c = 20.1°C) and of aniline in cyclohexane (t_c = 32°C). The mixture temperature was maintained constant within 0.05° (the solution was not stirred). The spectrum of depolarized scattering was excited with He-Ne laser radiation (λ = 6328 Å) polarized in the scattering plane; the scattered light, polarized perpendicular to the scattering plane, was observed at an angle of 90°. This light was analyzed with a Fabry-Perot interferometer with dispersion ranges 1.833 and 16.7 cm^{-1}. The variation of the spectrum of scattering by the anisotropy fluctuations is illustrated in Fig. 1, which shows the intensity distribution as a function of the frequency ν (reckoned from the exciting-line frequency) in the solution at three temperatures t (°C) for the mixture of nitrobenzene with n-hexane. When the critical lamination point is approached (from the side of the homogeneous phase), the Rayleigh line wing narrows down rapidly and at 0.25° from the critical point it practically coincides with the apparatus function (half-width $\Delta\nu_a = 3.8 \times 10^{-2}$ cm^{-1}). We note also that the half-width of the Rayleigh line width of the mixture ($\Delta\nu_a = 3.8 \times 10^{-2}$ cm^{-1} at 30° from the critical point) is much smaller than this half-width in pure nitrobenzene ($\Delta\nu$ = 0.36 cm^{-1} at the same

temperature). The picture observed in the aniline-cyclohexane mixture is qualitatively the same. As is well known, the Rayleigh line wing of many pure liquids, including nitrobenzene, can be described with satisfactory accuracy by a sum of two Lorentz contours[1)] with different half-widths $\Delta\nu_{1,2} = 1/\pi c\tau_{1,2}$, where τ_1 and τ_2 ($\tau_1 >> \tau_2$) are two anisotropy relaxation times. The nearby section of the wing, and consequently the longer anisotropy-relaxation time τ_1, is connected with the Brownian rotational diffusion [4 - 6] or with rotational jumps through large angles.

To trace the variation of τ_1 and τ_2 as the critical point is approached, we have plotted I^{-1} (I is the intensity) against the frequency squared ν^2. Since τ_1 and τ_2 differ greatly in magnitude, the plot of I^{-1} against ν^2 consists of two straight lines that meet in a transition region that occupies a relatively small spectral region. τ_1 and τ_2 were determined from the slopes of these lines [4, 5].

Plots of $\ln\tau_1$ and $\ln\tau_2$ against $\ln\varepsilon$ ($\varepsilon = (t - t_c)/T_c$, where T_c is the critical temperature in °K) are shown in Fig. 2. The character of these plots enables us to write $\tau_{1,2} = \tau_{1,2}^{reg} + \tau_{1,2}^{0}\varepsilon^{-\sigma_{1,2}}$, with $\sigma_1 = 0.62$, $\tau_1^0 = 5.9 \times 10^{-11}$ sec, $\tau_1^{reg} << 10^{-10}$ sec, $\sigma_2 = 0.66$, $\tau_2^0 = 4.6 \times 10^{-3}$ sec, and $\tau_2^{reg} = 3 \times 10^{-12}$ sec for the mixture of nitrobenzene with n-hexane. The accuracy of the critical exponents σ_1 and σ_2 is estimated by us at 10 and 30%, and the accuracy of $\tau_{1,2}^0$ at about 50%.

There is at present no theory of the Rayleigh line wing for the critical region, and we can hardly compare our critical exponents σ_1 and σ_2 with results of investigations of other phenomena near the critical point. The critical exponents σ_1 and σ_2 determined by us coincide, within the limits of the

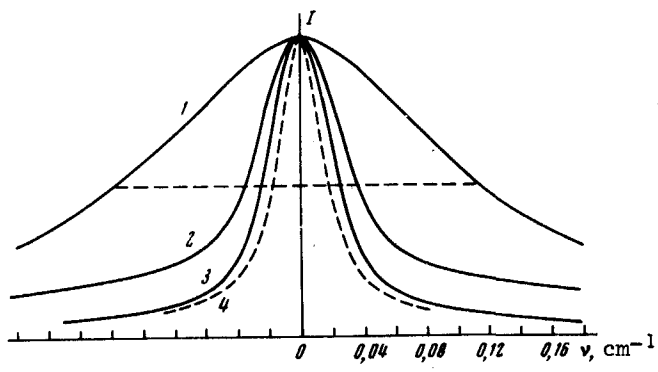

Fig. 1

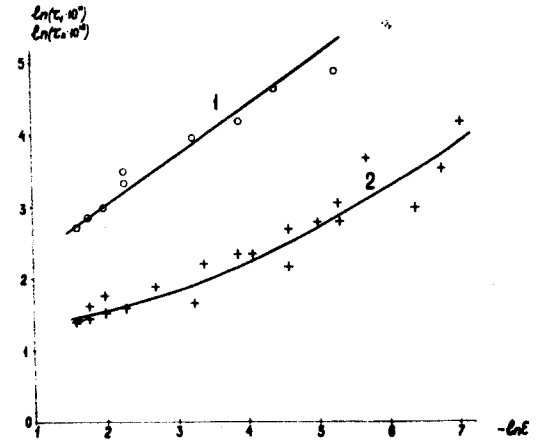

Fig. 2

Fig. 1. Intensity distribution in the Rayleigh line wing: 1 - nitrobenzene (t = 20°C); 2, 3 - mixture of nitrobenzene and n-hexane at $t - t_c = 11.55°$ and 1.55°, respectively, 4 - mixture of nitrobenzene and n-hexane at $t - t_c = 0.25°$ (has the same width as the apparatus function).

Fig. 2. Plots of $\ln\tau_1$ (circles) and $\ln\tau_2$ (crosses) against $\ln\varepsilon$ [$\varepsilon = (t - t_c)/T_c$] in a mixture of nitrobenzene and n-hexane. Solid lines 1 and 2 - results of calculation of $\tau_1 = \tau_1^0\varepsilon^{-\sigma_1}$ and $\tau_2 = \tau_2^{reg} + \tau_2^0\varepsilon^{-\sigma_2}$ (the parameters are defined in the text).

[1)] We neglect here the inertia effect [4, 5] which plays an important role at frequencies $\sim$30 - 120 cm^{-1}.

experimental errors, with the exponent $\gamma = 0.66$ characterizing the translational diffusion $D_t \sim \varepsilon^{\gamma}$ [7, 8]. It is not clear whether this agreement is accidental or not.

In the theory of Brownian motion, the coefficients of translational and rotational diffusion D_t and D_r are expressed by the well-known Einstein formulas $D_t = kT/6\pi\eta r$ and $D_r = kT/8\pi\eta r^3$, where r is the radius of the particle, η is the viscosity, and $\tau_1 = 1/6D_r$ is the anisotropy relaxation time. These relations were extended to include also molecular processes, and it was obtained in the theory of critical phenomena that $D_t = kT/6\pi\eta\xi$, where ξ is the correlation radius. It follows from our investigation that for rotational diffusion in the region of the critical point, either the formula for D_r with r replaced by ξ does not hold near the critical point, or else the correlation radius for the orientational motion differs strongly from the correlation radius for the translational motion, and one should thus assume the existence of another characteristic dimension.

All the questions raised here can be solved, in our opinion, only by investigating this phenomenon experimentally and theoretically. Such investigations can yield valuable information both on the behavior of substances near critical points and on the physical nature of the kinetic processes that lead to the appearance of a complex spectrum of depolarized scattering.

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OBSERVATION OF FERROMAGNETIC INTERACTIONS IN ANTIFERROMAGNETIC PEROVSKITES BY THE MOSSBAUER EFFECT

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It is known that indirect exchange interactions in oxides of transition metals are the main factor governing the antiferromagnetic mutual orientation of the magnetic moments of the cations. A positive (ferromagnetic) interaction has been predicted, for phenomenological considerations [1], only for the case of the $Fe^{3+} - O^{2-} - Cr^{3+}$ interaction (linear chain). Experimentally, however, no such phenomenon has been observed so far to our knowledge.

To observe the proposed interaction, we have investigated, by the nuclear gamma resonance (Mossbauer effect) method, the magnetic fields induced at Sn^{119} nuclei introduced in small amounts (2.5 at.%) as "observers" in the compound $LaFe_{1-x}Cr_xO_3$. To balance the valence, a suitable number of Ca^{2+} ions was introduced. In perovskite structures, the Sn^{4+} ions occupy the same octahedral positions as the magnetic cations. The Ca^{2+} ions enter into the rare-earth