

Temperature dependence of the spectrum of depolarized light scattering near the critical point of solution stratification

G. I. Kolesnikov, V. S. Starunov, and I. L. Fabelinskii

P. N. Lebedev Physics Institute, USSR Academy of Sciences

(Submitted June 8, 1976)

Pis'ma Zh. Eksp. Teor. Fiz. **24**, No. 2, 73-77 (20 July 1976)

It is established that in a solution of carbon disulfide in ethyl alcohol, in the region of the critical stratification temperature t_c , the wing of the Rayleigh line and the orientational part of the Raman-scattering (RS) line $\nu = 656 \text{ cm}^{-1}$ become abruptly narrower. A strong narrowing of three RS lines of nitrobenzene in a solution of nitrobenzene in *n*-hexane is observed in the region t_c .

PACS numbers: 78.30.Cp, 78.30.Ly

1. The purpose of this article is to present the results of a study of the temperature kinetics of the widths of the Rayleigh line wing^[1] (RLW) and of the depolarized Raman-scattering (RS) light^[2] in a carbon disulfide-ethyl alcohol ($\text{CS}_2\text{-C}_2\text{H}_5\text{OH}$) solution as the critical stratification temperature t_c of the solution is approached, and to report briefly the temperature dependence of the widths of the depolarized RS lines in a nitrobenzene-*n*-hexane solution. The strong narrowing of the RLW when t_c is approached in nitrobenzene-*n*-hexane and in *n*-dodecane- β , β' -dichlorodiethyl ether and the nonmonotonic character of this narrowing was observed earlier.^[3,4] In these solutions, which consist of rather complicated molecules, the temperature intervals in which the RLW are strongly narrowed alternate with sections in which there is practically no narrowing. In the solution $\text{CS}_2\text{-C}_2\text{H}_5\text{OH}$ ($t_c = -21.4^\circ\text{C}$) the RLW is determined practically entirely by the simpler linear molecule CS_2 , and CS_2 also has a de-

polarized RS line $\nu = 656 \text{ cm}^{-1}$ (with depolarization coefficient $\rho \sim 0.2$). Since the width of the RLW and the depolarized part of the RS are of similar nature [5-8] and are due to orientational motion of the molecules, this motion can be investigated by using either RLW or RS. In this and in other solutions with strongly critical opalescence this is particularly important, since if the RLW spectra are not properly reduced, then multiple scattering can greatly distort the measurement results, whereas this scattering exerts no influence whatever on the line width.

2. The RLW was investigated in a setup with a Fabry-Perot interferometer having a free spectral range 16.7 cm^{-1} . The scattered-light spectrum was scanned by varying the pressure in the interferometer chamber. The scattering was excited with an Ne-He laser ($\lambda = 6328 \text{ \AA}$) of 40–50 mW power. The RS was excited by an He-Cd¹⁴ laser ($\lambda = 4416 \text{ \AA}$) of 30–40 mW power and was investigated with a DFS-12 diffraction spectrograph (free spectral range 4.6 \AA/mm). In both cases, the scattering angle was 90° , the excited light was polarized in the scattering plane, and consequently only the depolarized part of the RS line was investigated. The scattered light was registered by the photon-counting method. After mixing the solution, the temperature was maintained for 4–6 hours accurate to $\pm 0.05^\circ$. The RSW results were reduced by the same method as in [4]. For each temperature we plotted the reciprocal intensity I^{-1} against the frequency squared $(\Delta\nu)^2$ and reduced that part of the spectrum on which the multiply-scattering light, having the same width as the apparatus counter, exerted no influence. According to an idea by Sobel'man, [5] which was further developed theoretically in [6] and experimentally confirmed [7-10], a part $\delta\nu_{op}$ of the half-width of the depolarized RS line is due to rotary motion of the molecules. By excluding the width of the apparatus function it is possible to write for the half-width¹⁾ of the RS line [6,7] $\delta\nu_{cr} = \delta\nu_{res} + \delta\nu_{op}$, where $\delta\nu_{res}$ is the "residual" half-width, which is practically independent of temperature, whereas $\delta\nu_{op}$ depends on the absolute temperature T and on the viscosity η in the same manner as the RLW half-width, namely $\delta\nu_{op} \propto T/\eta$. To determine $\delta\nu_{res}$ we plot $\delta\nu_{cr}$ against T/η . In critical mixtures far from t_c , just as in non-critical solutions and in pure liquids, [7] this plot is a straight line. Extrapolation

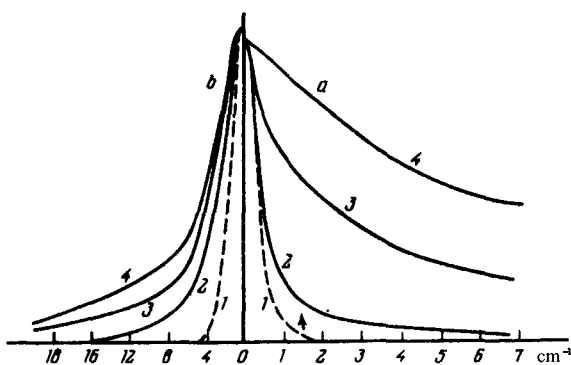


FIG. 1. Intensity distribution in the Rayleigh-line wing (a) and in the depolarized part of the CS_2 line $\nu = 656 \text{ cm}^{-1}$ (b) in a $\text{CS}_2 - \text{C}_2\text{H}_5\text{OH}$ solution at different temperatures: a) 1—apparatus function; 2— $\Delta t_c = 1.5^\circ$; 3— $\Delta t_c = 20^\circ$; 4— $\Delta t_c = 50^\circ$. b) 1—apparatus function; 2— $\Delta t_c = 0.4^\circ$ and 1.8° ; 3— $\Delta t_c = 5.6^\circ$; 4— $\Delta t_c = 44^\circ$.

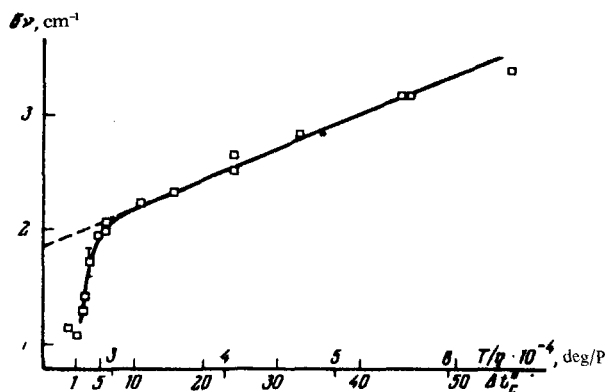


FIG. 2. Dependence of the half-width of the depolarized part of the $\nu = 656 \text{ cm}^{-1}$ line on T/η in the $\text{CS}_2 - \text{C}_2\text{H}_5\text{OH}$ solution.

tion of this line to $T/\eta \rightarrow 0$ yields $\delta\nu_{\text{res}}$ for the investigated substance, and consequently it becomes possible to determine $\delta\nu_{\text{op}}$ and the anisotropy temperature $\tau = (2\pi c \delta\nu_{\text{op}})^{-1}$.

3. Figure 1 shows the intensity distributions of the RLW (Fig. 1a) and of the depolarized part of the RS line (Fig. 1b) for several temperatures in the solution $\text{CS}_2 - \text{C}_2\text{H}_5\text{OH}$. We reduced the RLW in the frequency region above 1.5 cm^{-1} (marked by the arrow in Fig. 1a). It follows from Fig. 1a that even if the entire intensity at the maximum were due only to multiple scattering, it still could not influence the distribution of RLW intensity frequencies higher than 1.5 cm^{-1} , even at $\Delta t_c = t - t_c$ (t is the solution temperature). The half-widths of the RLW and of the depolarized part of the $\nu = 656 \text{ cm}^{-1}$ line are decreased by the same amount, $\sim 2.2 \text{ cm}^{-1}$, in the temperature interval from $\Delta t_c = 56^\circ$ to $\Delta t_c = 1^\circ$.

Figure 2 shows the dependence of the half-width $\delta\nu_{\text{cr}}$ of the RS line on T/η . It follows from Fig. 2 that in the temperature region from $\Delta t_c = 56^\circ$ to $\Delta t_c = 5^\circ$ the value of $\delta\nu_{\text{cr}}$ decreases linearly with decreasing T/η , and $\delta\nu_{\text{cr}}$ is sharply narrowed in the region $\Delta t_c = 5$ to 1.3° . Extrapolating the linear section of the plot in Fig. 2 to the value $T/\eta \rightarrow 0$ we obtain $\delta\nu_{\text{res}} = 0.85 \text{ cm}^{-1}$, which agrees, within the limits of experimental error, with $\delta\nu_{\text{res}}$ in pure CS_2 , as obtained by us in [10]. $\delta\nu_{\text{op}} = \delta\nu_{\text{cr}} - \delta\nu_{\text{res}}$, and from the relation indicated above we can find the temperature dependence of the anisotropy relaxation time τ .

Figure 3 shows a plot of $\ln\tau$ against $-\ln(\epsilon = \Delta t_c/T_c)$, T_c is the critical stratification temperature in $^\circ\text{K}$). The data were obtained from measurements of the RLW half-width (circles, triangles) and for measurements of the half-width of the depolarized part of the RS line (squares). As follows from Fig. 3, both methods of determining τ lead to the same results. It follows also from Fig. 3 that in the temperature interval in which τ varies rapidly ($\Delta t_c = 4.6 - 1.3$) this quantity changes by a factor of four, whereas the viscosity changes by only 5%, and in contrast to the solutions investigated in [4], that there is only one temperature interval in which the half-width or the anisotropy relaxation time varies rapidly.

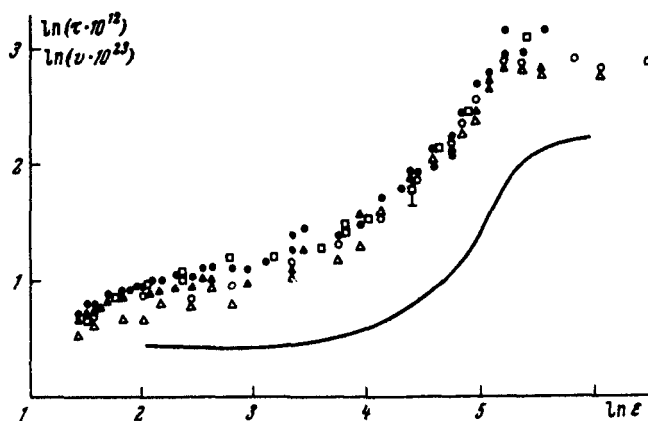


FIG. 3. Dependence of $\ln(\tau \cdot 10^{12})$ on $-\ln \epsilon$ [$\epsilon = \Delta t_c / T_c$] in the solution $\text{CS}_2 - \text{C}_2\text{H}_5\text{OH}$: Δ, \triangle —Rayleigh-line wing, the scattered light is polarized in the scattering plane, \bullet, \circ —Rayleigh-line wing, the scattered light is polarized perpendicular to the scattering plane, \square —the depolarized part of the $\nu = 656 \text{ cm}^{-1}$; solid line— $\ln V (V = kT\tau/\eta)$ against $-\ln \epsilon$ obtained by averaging the dependence of $\ln \tau$ on $-\ln \epsilon$.

We have also investigated the temperature kinetics of three RS lines of nitrobenzene $\nu_1 = 610 \text{ cm}^{-1}$ ($\rho = 0.87$), $\nu_2 = 1345 \text{ cm}^{-1}$ ($\rho = 0.30$) and $\nu_3 = 1586 \text{ cm}^{-1}$ ($\rho = 0.55$) in a nitrobenzene—*n*-hexane solution ($t_c = 20^\circ \text{C}$) under the same experimental conditions as the RS in $\text{CS}_2 - \text{C}_2\text{H}_5\text{OH}$, and found that as t_c is approached all three lines are strongly narrowed down, to approximately the same extent as the RLW in this solution.^[4] These results confirm fully the existence of the effect of strong narrowing of the RLW^[3,4] and show that in^[11], where no RLW narrowing was observed in a nitrobenzene—*n*-hexane solutions, the experimental method used for the investigation of the temperature dependence of the RLW was inadequate. We note that different RS lines of nitrobenzene in the nitrobenzene—*n*-hexane solution narrow down in different temperature intervals, and this, as well as the nonmonotonic narrowing of the RLW^[2], suggests that the slowing down of the rotational motion of the molecules about the different axes as t_c is approached can occur in different temperature intervals.

A more detailed exposition and discussion of the experimental results will be presented elsewhere.

In conclusion, the authors thank V. P. Zaitsev for help with the experiment.

¹The half-width is defined here as half the width of the contour at a height equal to $I_{\text{max}}/2$, where I_{max} is the intensity at the maximum.

¹I. L. Fabelinskiĭ, *Molekulyarnoe rasseyaniye sveta* (Molecular Scattering of Light), Nauka, 1965 [Plenum, 1968].

²K. W. F. Kohlrausch, *Ramanspektren*, Akad. Verlag, Leipzig 1943 (Repr. Edwards Bros.), Russ. transl. IIL, 1952.

- ³A.K. Atakhodzhaev, L.M. Sabirov, V.S. Starunov, I. L. Fabelinskiĭ, and T.M. Utarova, Pis'ma Zh. Eksp. Teor. Fiz. 17, 95 (1973) [JETP Lett. 17, 65 (1973)].
- ⁴I. L. Fabelinskii, V.S. Starunov, A.K. Atakhodzaev, L.M. Sabirov, and T.M. Utarova, Opt. Commun. 15, 432 (1975).
- ⁵I. I. Sobel'man, Izv. Akad. Nauk SSSR Ser. Fiz. 17, 554 (1953).
- ⁶K.A. Valiev, Zh. Eksp. Teor. Fiz. 40, 1832 (1961) [Sov. Phys. JETP 13, 1287 (1961)].
- ⁷A.V. Rakov, Tr. Fiz. Inst. Akad. Nauk SSSR 27, 111 (1964).
- ⁸A. I. Sokolovskaya, ibid., 63.
- ⁹G. I. Zaitsev and V.S. Starunov, Opt. Spektrosk. 19, 893 (1965)
- ¹⁰F. J. Bertoli and T.A. Litovitz, J. Chem. Phys. 56, 404 (1972).
- ¹¹D. Beysens, A. Bourgou, and G. Zalczer, Opt. Commun. 15, 436 (1975).