

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

G. A. Kazunina and D. V. Alekseev

Kemerovo State University

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A strong narrowing of the $\nu = 894 \text{ cm}^{-1}$ polarization line of acetic acid was observed in a solution of cyclohexane in acetic acid in the region of the critical stratification temperature.

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1. The first studies of the temperature kinetics of the depolarization of the lines of Raman scattering (RS) of light in stratifying solutions^{1,2} have revealed a strong narrowing of the orientational part $\delta\nu_{\text{or}}$ of the RS line when the stratification temperature t_c is approached from the direction of the homogeneous phase. This narrowing was attributed to an increase of the relaxation time τ of the anisotropy in the relation obtained by Sobel'man³ for $\delta\nu_{\text{d.or}}$ as a function of τ .

We have investigated the temperature dependence of the RS line widths in a stratifying solution of cyclohexane in acetic acid ($t_c = 4.8^\circ\text{C}$) and found that besides the $\nu = 1029 \text{ cm}^{-1}$ depolarization line of cyclohexane, the acetic-acid $\nu = 894 \text{ cm}^{-1}$ polarization line due to torsional oscillations of the OH group⁴ is also subject to strong narrowing (this line is also active in the IR absorption spectrum). According to Ref. 3, the rotational motion of the molecules does not influence directly the widths of the polarized lines.

2. Since the $\lambda = 894 \text{ cm}^{-1}$ line is active in the IR absorption spectrum (i.e., the corresponding vibration of the molecule induces a dipole moment d), while the molecules of acetic acid have a constant dipole moment $D = 1.63 \text{ D}$,⁵ the strong narrowing of this line can be explained by assuming that the rotational motions of the molecules influence the line width indirectly, via vibrational-excitation relaxation due to the dipole-dipole interaction. According to Ref. 6, that part of the half-width of the polarization line which depends on the absolute temperature is

$$\delta\nu_{\text{p.or}} \sim D^2 d^2 \left\{ (\nu\tau)^{-1} + \frac{\sqrt{3}}{2} (\nu\tau)^{-1/2} \right\} \quad (1)$$

whereas for a depolarized line we have $\delta\nu_{\text{d.or}} = (2\pi c\tau)^{-1}$.³ It is seen therefore that when t_c is approached (when τ increases) the temperature dependence $\delta\nu_{\text{p.or}}$ is determined principally by the second term in the curly brackets. If we approximate the behavior of $\delta\nu_{\text{p.or}}$ and $\delta\nu_{\text{d.or}}$ near t_c by power-law functions

$$\delta\nu_{\text{d.or}} \propto \epsilon^{\sigma_d}; \quad \delta\nu_{\text{p.or}} \sim \epsilon^{\sigma_p}; \quad \epsilon = (T - T_c) / T_c$$

then, since $\tau \propto \epsilon^{-\sigma}$ (Ref. 2), it should follow from the dependence of the half-widths $\delta\nu_{\text{d.or}}$ and $\delta\nu_{\text{p.or}}$ on the relaxation time τ that the ratio of the exponents is $\sigma_d/\sigma_p \approx 2$.

Raman scattering was excited with an LG-31 helium—cadmium laser ($\lambda = 4416 \text{ \AA}$) and was registered with a DFS-12 spectrometer (dispersion 4.6 \AA/mm). The temperature of the solution was maintained constant within $\pm 0.1^\circ$ for 4–5 hours. The instrumental function was Gaussian with half-width 1.5 cm^{-1} .

Figure 1 shows the temperature dependence of the half-widths of the investigated

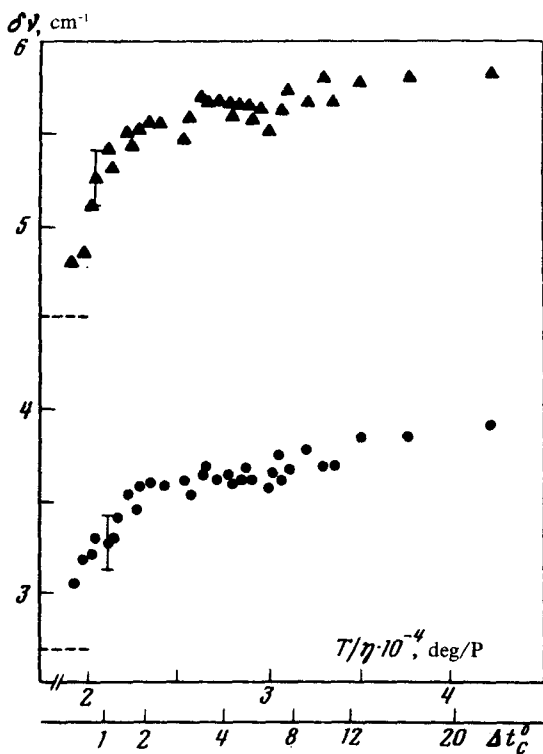


FIG. 1. Dependence of the half-width of the depolarized $\nu = 1029 \text{ cm}^{-1}$ line (\blacktriangle) of cyclohexane and of the polarized $\nu = 894 \text{ cm}^{-1}$ line (\bullet) of acetic acid on T/η in a solution of cyclohexane in acetic acid. The dashed lines show the "residual width."

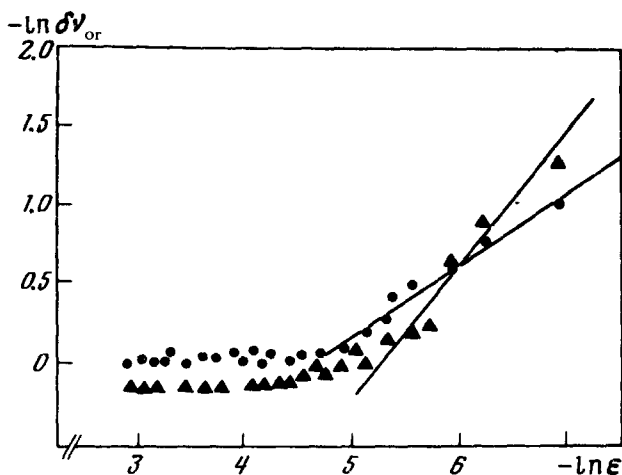


FIG. 2. Determination of the exponents σ_p and σ_d . The circles and the triangles represent respectively the dependences of $-\ln \delta \nu_{p,or}$ and $-\ln \delta \nu_{d,or}$ against $-\ln \epsilon$.

lines, referred to an ideal spectral instrument. The reduction of the spectra of the depolarized RS was carried out in the same manner as in Refs. 1 and 2, namely, the half-width of the line was represented in the form $\delta\nu = \delta\nu_{res,d} + \delta\nu_{d,or}$, where the "residual" width was determined by extrapolation, to infinite viscosity η of the linear section of the dependence of the half-width $\delta\nu$ on T/η in the region $t - t_c > 10^\circ$. The "residual" width of the polarized line was determined in the following manner: the anisotropy relaxation time $\tau \sim T/\eta$ and the temperature dependence of the half-width $\delta\nu_p$ were approximated far from t_c by the expression (cf. (1))

$$\delta\nu_p = \delta\nu_{p,res} + \alpha(T/\eta)^{1/2} + \beta(T/\eta)$$

whose coefficients were determined by least squares from measurements of the half-widths far from the critical temperature ($t - t_c > 10^\circ$). The exponents σ_d and σ_p were determined from the linear section, adjacent to t_c , of the plot of $-\ln\delta\nu_{or}$ against $-\ln\epsilon$ (Fig. 2). The obtained exponent ratio $\sigma_d/\sigma_p = 1.8 \pm 0.3$, confirms, in our opinion the proposed explanation of the strong narrowing of the polarized $\lambda = 894 \text{ cm}^{-1}$ line of acetic acid.

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