

Rotational Motion of Molecules and Structural Transitions in Liquid Pyridine

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Abstract

The temperature dependence of the anisotropic component intensity of molecular scattering of light and the contour shape of the anisotropic part of scattering have been measured. The anomalous behavior of the integral intensity of the anisotropic component of molecular scattering of light on temperature has been established. It has been shown that the regularities observed in scattering can be interpreted based on a mechanism of hindered rotation of molecules with taking into account the specifics of intermolecular interaction in pyridine.

INTRODUCTION

The intermolecular spectra can be a valuable source of information on the specifics of condensed matter since they reflect the features of molecule motion, intermolecular interaction and temperature changes in the structure of matter.

A theory of scattering in gases can be considered as complete. The phenomenon itself serves as a main method for determining the components of the polarizability tensor of molecules.

A theory of isotropic scattering associated with the density functions is also largely completed. The phenomenon can be used to determine a number of characteristics of a liquid for high frequencies (compressibility, hypersonic speed, etc.). There are papers [1-3] where a principal option of calculating a space-time molecular correlative function of the scattering system on the basis of accurate measurements of the contour lines of isotropic scattering was shown.

The situation with the theory of anisotropic scattering in a liquid is different. The difficulty in constructing a rigorous theory is that it is necessary to consider intermolecular interaction and, first of all, correlation of molecule orientation caused by this interaction [4,5]. The theory ignoring this correlation ("gas" theory) is in contradiction with the experimental values of the scattering intensity and, even more, cannot explain the temperature dependence of scattering intensity.

Analysis of available papers [4-10] shows that despite a significant amount of theoretical and experimental studies this problem cannot be considered as resolved. This is confirmed, in particular, by the annually increasing number of publications devoted to studying the intermolecular interactions and their effect on spectra, which is evidence of growing interest in this problem. The latter is not accidental since the study of the spectra of a system of interacting molecules is, in principle, a powerful means of studying, on the one hand, the nature of these interactions and, on the other one, the spectroscopic and other relaxation parameters of molecules that make up this system.

The study results of the temperature changes in the anisotropic component of molecular light scattering (ACMLS) in pure pyridine C₅H₅N are presented in this paper. In accordance with the goals and objectives of the study, the possibility of obtaining information on the nature of the

temperature behavior of the dynamics of the intermolecular interaction of molecules and on its structural changes has been analyzed.

EXPERIMENTAL

The ACMLS spectra were measured with an experimental setup based on a high-transmission diffraction spectrometer DFS-12 having a grid of 1200 line/mm. The setup is intended for recording the spectra of weak radiation in an automatic mode. The methodological part differs little from that described in [11,12]. The He-Ne laser (radiation wavelength 628 nm) was used as a source of radiation. Pyridine was refined by triple distillation. After refining, the pyridine samples were sealed in cuvettes under pressure below atmospheric one. The cuvette with pyridine was placed in a thermostat; its electronic scheme allows temperature stabilization within accuracy of not more than $\pm 0.5^{\circ}\text{C}$. The principal scheme is presented in Fig. 1.

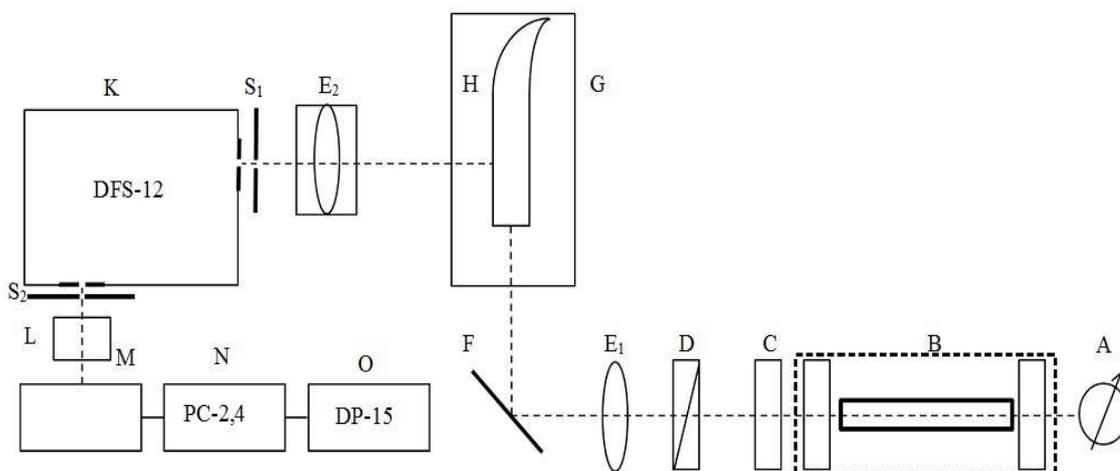


Fig. 1. The scheme of the experimental setup for photoelectric measurements of the anisotropic component of molecular light scattering: A – the semiconductor photodiode; B – the He-Ne laser; C – the $\frac{\lambda}{4}$ plate; D – the Nicol prism; E₁ – the focusing lens ($F = 150\text{ mm}$); Z – the reflective mirror; G – the high temperature furnace; H – the vessel with fluid under study; E₂ – the condenser; S₁, S₂ – the input and output slits; K – the spectrometer DFS-12; L – the PMT; M – the common-collector amplifier; N – the photon counter; O – the digital printing.

Laser radiation B was focused into a cuvette H with a liquid under study by a capacitor E₁ with a focal length of 150 mm. Radiation scattered by the cuvette at an angle of 90° was directed by the capacitor E₂ to the input slit S₁ of the spectrometer. The ACMLS spectra were studied within the temperature range from ~ 20 to $\sim 150^{\circ}\text{C}$.

RESULTS AND DISCUSSION

The results of experimental studies have demonstrated that the ACMLS contour is well represented by a superposition of two Lorentz components (curves a, b, c). This is illustrated in Fig. 2 where in the coordinates $(\frac{1}{I})$ of v^2 the two regions of straightening are clearly visible.

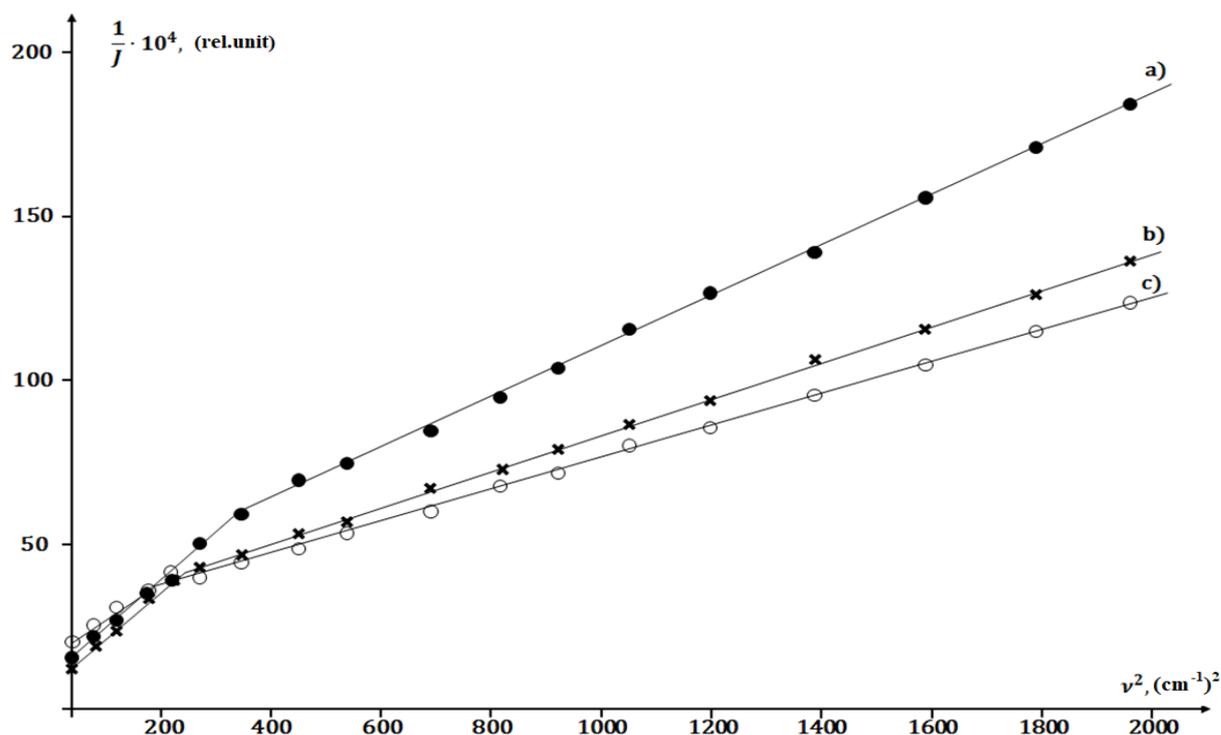


Fig. 2. The inverse spectral density of the ACMLS line contour in the pyridine molecule as a function of the frequency square for temperature: a) 20 °C; b) 50 °C; c) 100 °C

The observed contour of the scattering line is a sum of the two Lorentz lines within the frequency range from 0 to 40-50 cm^{-1} , with the boundary of about 17 cm^{-1} at room temperature. Under liquid heating, the inflection boundary moves to low frequencies and this boundary near 10 cm^{-1} for temperature equal to 100 °C. As the temperature changes, the shape changes. A change in the contour shape with temperature increase is associated with a change in both the weight and the half-width of the Lorentz components.

We consider a mechanism proposed earlier in [13], namely the Lorentz components are associated with hindered rotation of molecules (IRM) relative to the principal axes of inertia moments. Due to the independence of axis rotation, caused by molecule rotations, the fluctuations of anisotropy of elementary volumes of scattered will be independent as well. Therefore, light scattering will consist of three incoherent components having the intensity determined by the molecule anisotropy in the plane perpendicular to the corresponding axis of the inertia ellipsoid and by the degree of correlation of molecule orientation. For most simple molecules, the axis of inertia coincides with that of polarizability. Thus, the anisotropy of the molecule plane perpendicular to the rotation axis is equal to the difference of the main values of polarizability along the other two axes. Neglecting correlation (“gas” approximation), we can define the weights of the contours α_i by means of the main values of the components of the tensor of molecule polarizability.

$$\alpha_i \approx \alpha_i^{gas} = \frac{(\alpha_k - \alpha_j)^2}{2g^2} \quad (1),$$

where $g^2 = \frac{1}{2}[(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2]$ is the degree of molecule anisotropy.

The structure of the pyridine molecule allowed assuming that the half-width of the Lorentz contour σ_2 associated with rotation around the axis passing through the substituted top-points of

the benzene ring is to be much greater than the half-widths of the two other components. Calculated in the “gas” approximation according to (1) for pyridine, a theoretical value of α_3^{theor} of the weight (contribution) of the contour associated with rotation around the third axis (axis of symmetry) is much less than α_2 . The results of approximating the experimental contour of the ACMSL line with two Lorentz functions within the frequency range from 0 to 50 cm^{-1} are shown in Table 1.

Table 1.

Substance	T $^{\circ}\text{C}$	σ_1 , cm^{-1}	σ_2 , cm^{-1}	$\tau_1 \cdot 10^{12}$, s	$\tau_2 \cdot 10^{12}$, s	α_1	α_2	α_2^{theor}	α_3^{theor}
$\text{C}_5\text{H}_5\text{N}$	20	2.10	11.50	2.50	0.50	0.58	0.42	0,58	0,02
	50	3.50	11.80	1.50	0.40	0.53	0.47		
	80	4.80	12.00	1.10	0.40	0.50	0.50		
	100	5.20	12.20	1.0	0.39	0.45	0.55		
	150	5.80	12.80	0.90	0.38	0.40	0.60		
Statistical error	± 0.5	± 0.10	± 0.15	± 0.04	± 0.04	± 0.02			

The ACMSL contour complexity requires maximum objectivity for the experimental data to be treated. For this purpose, first of all, it is necessary to develop a technique of decomposing an experimental contour of the scattering line into components. We developed an algorithm of problem solving by a method of sequential approximations and decomposing an experimental contour into two Lorentz components [10]. According to these ideas, the half-widths of the Lorentz components are defined by relaxation times of rotation motion relative to the corresponding axes and the contour weights are to be close to 0.5 for molecules having a symmetry axis (rotation relative to the symmetry axis is optically inactive), approaching this value with the increase in temperature (due to lower correlations of molecular orientations). The analysis results of this model were earlier confirmed by measurements of benzene and its derivatives [6-13]. The data on pyridine, as seen from the table, also confirm this point of view.

As seen from Table 1, for pyridine there is a discrepancy in the number of the ACMSL contour lines from the IRM model. The experimental contour comprises two Lorentzians while the IRM model for liquids such as pyridine with asymmetric molecules predicts three ones. Possible reasons for this discrepancy are:

- a method of decomposing an experimental contour into components (our method allows experimental contour decomposition into two components only);
- a very small weight of the third contour as compared to other ones ($\alpha_3^{\text{theory}} = 2\%$). The third contour is difficult to separate from the first one so the contour decomposition of the ACMSL line into two components rather than into three Lorentz ones can be considered as a fairly reasonable approximation.

Specificity of pyridine molecules most manifests itself in the temperature dependence of the integral intensity. The temperature dependence of the general integral intensity of ACMSL is shown in Figure 3. The results are corrected for the temperature behavior of the refraction index of pyridine.

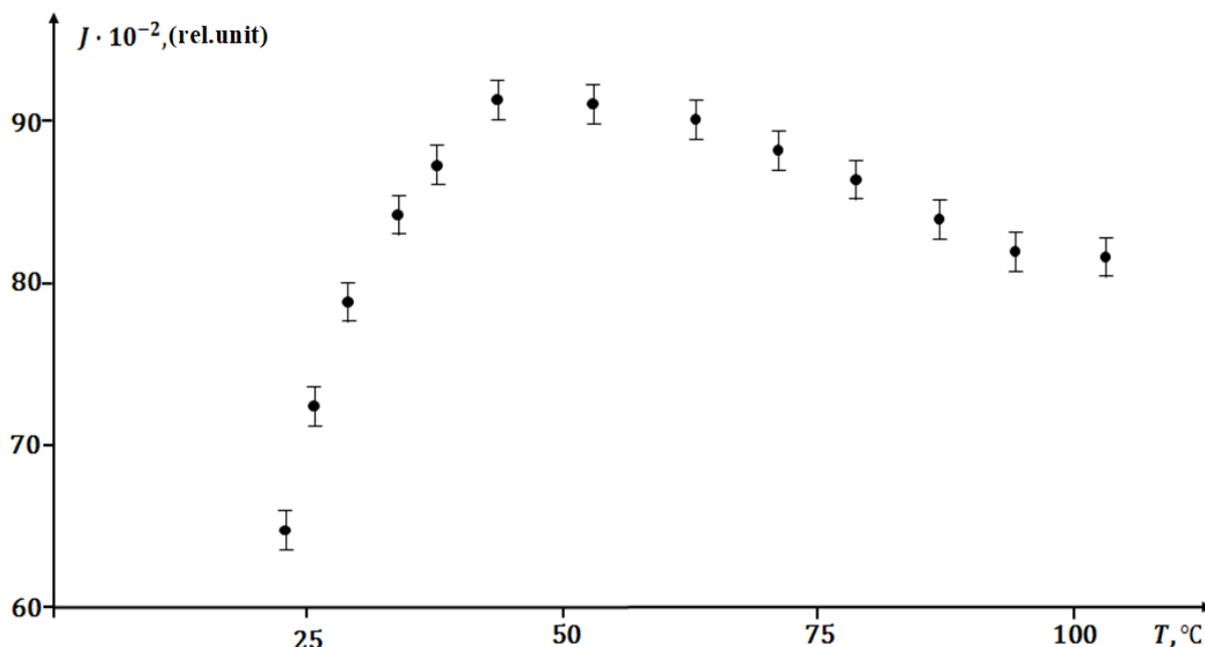


Fig. 3. The temperature dependence of the integral intensity of ACMSL in the pyridine molecule.

The refraction index was measured within the same temperature range as the ACMSL spectrum according to the procedure [14,15]. It was found that the refraction index within the measured temperature range monotonically decreases without any special deviations. As seen in Fig. 3, the intensity strongly depends on temperature (up to 40°C it increases, then decreases). Such a dependence of the integral intensity on temperature can be explained in the framework of the theory [16] since this theory is applied to only axisymmetric molecules and there are no direct calculations of the correlation factor for individual components. Most probably, an increase in the intensity within the range from room temperature up to 40°C and its further decrease for temperature above should be associated in liquid with the phenomenon of structural relaxation leading to destructing short-range order correlation.

This is due to the fact that, according to modern concepts, liquids have a specific short-range orientation and coordination order different from an existing solid state. Thus, the above-observed results are evidence of the effect of liquid structure on the scattering characteristics and of the strong influence of temperature on structures.

The possibility of a macroscopic manifestation of structural transitions in the liquid phase was also considered in [17]. Probably, the relatively small dipole moment of pyridine provides a less stable structure of the short-range order and this results in large fluctuations of molecule anisotropy.

CONCLUSION

It should be noted that the available theories differ not only in calculation formalism, but most importantly in scattering mechanisms: Brownian rotational diffusion, Brownian rotational motion plus Brownian vibratory motion, shift deformation, hindered rotation, rotational diffusion (Debye model) and “jump” diffusion, etc. Of course, the above-stated mechanisms exist and contribute to the ACMSL spectrum. It is necessary to establish the main mechanisms under the specific experimental conditions. It is reasonable to raise the question of the contributions of each

of them to the scattering spectrum.

Our studies are unambiguous evidence of structural changes in liquids associated with short-range order rearrangement. Our studies also indicate the need to take into account the liquid microstructure for describing scattering phenomena. The study results allow us to take a fresh look at the nature of anomalous changes in the integral intensity of ACMSL.

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