Intermolecular dynamics of condensed state: study of temperature effect on anisotropy relaxation by vibration spectroscopy

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Intermolecular Dynamics of Condensed State: Study of Temperature Effect on Anisotropy Relaxation by Vibration Spectroscopy

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Abstract

As a result of the experimental study of the spectra of anisotropic scattering of light, a character of orientation movement of molecules in aromatic hydrocarbons has been analyzed. The obtained results have been interpreted from the viewpoint of a model of inhibited rotation and the contributions of the rotational and vibrational degrees of freedom to a molecule spectrum have been estimated. With increasing temperature of liquids under study and approaching a critical state, the rotational degrees of freedom "freeze", and the vibrational degrees have become more significant.

Keywords: *Light scattering, anisotropic scattering, half-width, relaxation time, anisotropy, orientation, vibration, degree of freedom, critical temperature.*
PACS classification number: *33.20.Fb, 78.35.+c.*

1 Introduction

The spectra of molecular scattering of light (MSL) provide extensive and diverse information on the finest phenomena that can be found under interaction of radiation with a matter. Molecular scattering of light in a matter can be divided into two parts: the first one is associated with density fluctuation (isotropic scattering) and the second one with fluctuation of anisotropy (anisotropic scattering).

A theory of isotropic scattering in liquids has been basically finished. The phenomenon can be used for defining a number of the characteristics of liquid for high frequency (compressibility, hypersonic speed, etc.). The situation with a theory of anisotropic scattering in liquid is different. The difficulty in constructing a rigorous theory is connected with the fact that it is necessary to take into account the intermolecular interaction and, first of all, the correlation of molecular orientation caused by this interaction. A theory that neglects this correlation (a gas theory) gives the values of the scattering intensity different from the experimental ones and, what is more important, cannot explain the temperature dependence of scattering intensity. In the work [1], the theory of anisotropic scattering is constructed based on the consideration of fluctuations of anisotropy as a rotational Brownian motion of molecules. In the work [2], along with fluctuations caused by the Brownian motion, the influence of fluctuations associated with the elastic vibrations of molecules is also considered. Such a statistical approach in the theory takes into account molecular interactions.

The authors of the works [1, 2] obtained the interesting results mainly for a contour of scattered light. However, it should be noted that these theories mainly consider the macroscopic parameters (viscosity, elasticity, diffusion coefficient), which significantly reduces the value of these works for scattering to be used as a source of information about the liquid structure and the dynamics of molecules in liquid.

The above theories [3]-[8] have a common point that is associated with a theory of experimental techniques and system dynamics equally measured in light scattering. One important disadvantage of these theories is that they are too simplified to determine fluid dynamics, although the phenomenology for the part of light scattering is correct.

Since all the above-mentioned theories are phenomenological, it is difficult to decide which one will provide a "correct" description of the spectra.

In the work [9], a dynamic method of light scattering is used to measure the polarized and anisotropic parts of MSL. These results make it possible to extract information on the structure of relaxation processes of rotational motions and can provide information on translations of rotations by compounds and molecular phenomena reoriented into a liquid state like diphenyl methane molecules. The authors provide a detailed formula of calculation but this formula is valid only in the region of low viscosity.

In the work [10], the optical forces with radial anisotropy were studied using the generalized Mie theory and Maxwell theory by integrating the stress tensor for an incident plane wave, and we can see that both analytical and numerical results show anomalous models of the Rayleigh law instead of the known dependence on wave number and size, i.e. $F \approx k_0^4 a^6$.

When the traditional light sources were replaced by laser ones with an intense emission line and with a degree of monochromaticity, the situation with observing a spectrum of the anisotropic component scattered in liquids also changed significantly.

The authors of works [11]-[14] used a picosecond laser of light pulses and observed the kinetics of the optical Kerr effect in several liquids. The results are in good agreement with the Debye relation between the orientation relaxation time and the macroscopic viscosity.

In the work [15] the spectra (up to 200 cm^{-1}) of Rayleigh scattering of light were analyzed in three liquids with symmetric molecules, i.e. in cyclopropane, allene, and benzene. It was shown that the results obtained cannot be interpreted only by orientational fluctuations, but can show good agreement with the vibrational movements of molecules as a damped oscillator.

In the work [16], the authors used anisotropic hyper-Rayleigh scattering to study the intermolecular interaction in liquid nitrobenzene. By comparing the degree of depolarization in the ratio of the second harmonic of the scattered light for pure nitrobenzene and for a mixture of nitrobenzene with methanol, the authors showed that in liquid nitrobenzene there is a coherent component of the hyper-Rayleigh scattering and that this coherent component can completely disappear with a sufficiently high dilution of methanol nitrobenzene, i.e. scattering is fully associated with the polarization of the substance molecules. The results once again justified the general

practice of determining molecular hyper polarizability using hyper-Rayleigh scattering of light.

In the works [17, 18], the possible causes of discrepancies between the theoretical and experimental results in vibrational relaxation in some benzene derivatives were analyzed.

Especially for the gas phase, some relations were observed between relaxation time, absorption, and substance structure, i.e., for gases, the larger the compound molecule, the shorter the relaxation time. For liquids, the larger the substituent molecule, the shorter the relaxation time and the lower the absorption of the low-frequency region.

It was also observed that there is a correlation between the acoustic properties of dipole moments for saturated and unsaturated compounds. Nevertheless, the authors could not give a full explanation of these dependencies, and they require further physical studies of such cyclic and heterocyclic compounds.

With the use of a combination of different light scattering methods (double monochromator, Fabry-Perot interferometer, photon correlation spectroscopy), the spectra of anisotropic scattering of light were measured for a number of glass-forming substances within the temperature range from boiling temperature ($T \leq 440$ K) to temperature of glass transition T_{gl} in [19]-[21].

As shown by the studies conducted around the world, a leading place in the study of relaxation processes in the liquid phase is occupied by spectroscopic methods, among which the MSL spectroscopy, especially its anisotropic component (AC), possess a definite advantage.

The creation of a closed theory of the liquid state of a substance is undoubtedly an urgent task, primarily because it can be used to obtain reliable data on liquid structure, on the effect of thermal motion of molecules on this structure. The thermal motion of molecules in a liquid determines their basic physical properties and macroscopic characteristics. Its description is based on a number of theoretical models created; but they are so far from being perfect that for polyatomic compounds they make impossible to calculate most of the characteristics. The available experimental data are also contradictory and incomplete. Therefore, we have done a lot of work described in this paper.

The purpose of this work is to study the manifestation of changes in the structure of aromatic hydrocarbons with methyl and halide substituents, develop optical methods of analysis, and determine the physical mechanisms of relaxation processes associated with intermolecular interactions in the radiation spectrum.

2 Equipment and experimental technique

For the anisotropic component of molecular scattering of light (ACMSL) in liquids to be studied within the wide range of frequency and high temperatures, it is necessary to have the following equipment:

- a cuvette suitable for working under conditions close to critical parameters and giving the smallest "black background";

- a device for uniform heating of a substance with the possibly minimal gradient of temperature along the cuvette length;

- a high-resolution spectral instrument with sufficient aperture;

- a source of excitation for contour detection (power, monochromaticity);

- substances (liquids) with critical parameters suitable for study;

- methods of substance cleaning and cuvette filling;

- methods of experimental data processing (not only statistical treatment and accounting for hardware distortion, but also, mainly, processing making it possible to objectively and possibly completely compare experimental data with those of scattering theories).

In the study of molecular light scattering, special requirements are imposed on a spectral instrument. This is due, firstly, to the smallness of the scattering coefficient ($R \sim 10^{-6}$), and secondly, when measuring within a wide spectral range ($\sim 300 \ cm^{-1}$), the intensity change ($\Im_0 / \Im_{wing}$) occurs no less than three orders. Therefore, the spectral instrument must have:

a) good aperture and resolution of ~ 10;

b) no scattered light in the instrument, which is especially important for measurement of the far wings of the scattering contour.
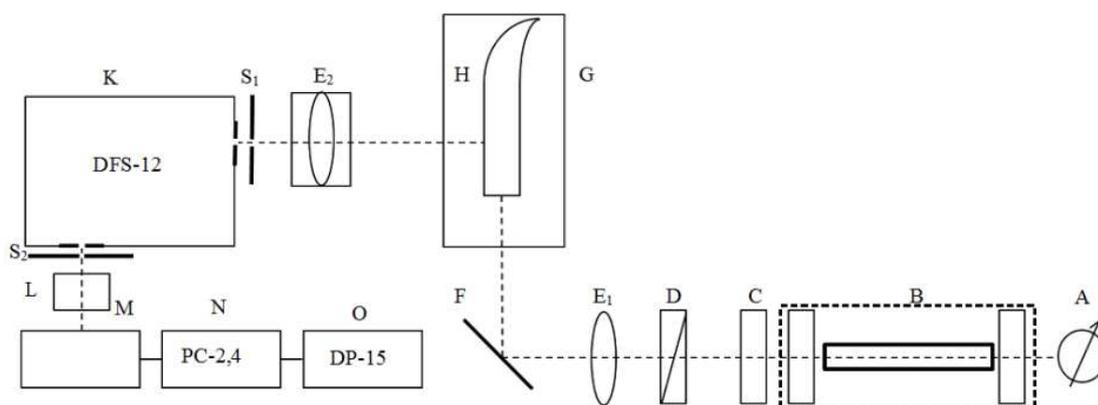

Figure 1: The scheme of the experimental setup for photoelectric measurement of far parts of the spectra of the anisotropic component of molecular scattering of light: A - semiconductor photodiode; B - He-Ne laser; C - plate $\lambda/4$; D - Nicolas prism; E_1 - focusing lens (F=150 mm); Z - reflective mirror; G - high-temperature heater; H - cuvette with a liquid under study; E_2 - condenser; S_1, S_2 - input and output slit; K - spectrometer DFS-12; L - photoelectric multiplier; M - emitter repeater; N - photon counter; O - digital printing.

Therefore, our measurements were performed with the DFS-12 devices (Fig. 1). The optical parameters of the diffraction spectrometer DFS-12 have the following characteristics:

* focal length of specular parabolic lenses - 820 mm;

* diffraction grating (number of strokes per 1 mm, first order) - 1200;

* relative hole of collimators 1: 5.3;

* linear dispersion at the exit slit - 5 / mm;

* the size of the shaded part is 150-140 mm.

Laser radiation B was focused into a cuvette H with a liquid under study by the lens E_1 with a focal length of 150 mm. The scattered light from the cuvette was reflected by the capacitor E_2 to the input of the slit S_1 of the spectrometer. Due to the double decomposition, the light exiting the spectrometer K is more monochromatized and the spectrometer dispersion doubles.

For the study of the far parts of the anisotropic component of the spectrum where the intensity decreases with respect to the maximum by several orders of a magnitude, the issue of increasing the sensitivity of the entire setup becomes crucial. The scanning receiving and recording part of the setup was modified [22].

As known, for quantitative measurements of the parameters of the scattering line contour, an essential role is played by the constancy of the light source intensity. As the exciting light, we used the argon laser radiation LG-106 M-1 (B) polarized in the scattering plane with a wavelength $\lambda = 488$ nm and a power of up to ~ 1 W.

All parts of the lighting system were thoroughly blackened to prevent "parasitic" light from entering the spectrometer. Moreover, the entire projection system together with the polarizer was placed in the hoods that were impervious to the constructed light.

The measurements were performed within the wide range of temperature from the room one to those close to critical temperatures for each of the studied substances.

The study objects were mainly selected, on the one hand, by the similar structure (the base is a benzene ring) and, on the other one, by the difference in the molecule shape and the nature of substitution.

In addition, the substances in which the temperature effects are studied should satisfy the following requirements: transparency within the visible region of light; the wide temperature range for a substance in the liquid state; chemical resistance of the liquid to the light and temperature influences; large anisotropy (clear spectroscopic manifestation of orientational relaxation of molecules in MSL); no dipoles or low dipoles, which eliminates the possible influence of additional orienting interaction.

The different nature of the attachment of methyl and halide groups to the benzene ring makes them interesting objects for the study of the substituent effect on a character of the relaxation processes of molecules in the liquid phase. The anisotropy of the shape and polarizability of mono- and para-substituted benzene molecules changes in accordance with a certain regularity. The light scattering characteristics obtained in this way allow a more detailed comparison of the theoretical and experimental values of many parameters.

The following substances were studied: benzene C_6H_6, bromobenzene C_6H_5Br, toluene $C_6H_5\left(CH_3\right)$, aniline $C_6H_5NH_2$ and carbon tetrachloride CCl_4.

In the study of molecular scattering, special attention should be paid to the purity of objects. The "parasitic" illumination associated with the presence of traces of water and various impurities and different particles in the studied substances leads to a distortion of the pattern of intermolecular interactions, a change in the anisotropic scattering spectra and, consequently, errors in the interpretation of these changes and

the quantitative results obtained on their basis. In this regard, all the substances we used were thoroughly cleaned, dried and dust free.

Each substance, depending on the purity grade of the initial product, was cleaned differently, according to [23]-[25].

The complexity of the line contour of the ACMSL requires maximal objectivity when processing the experimental data. For this, first of all, it is necessary to develop a technique for decomposing the experimental contour of the scattering line into components.

The objective decomposition of the experimental spectrum into three contours with simultaneous exclusion of the hardware function is an almost insoluble problem. We have compiled an algorithm for solving this problem by a method of successive approximations and decomposition of an experimental contour into two Lorentz components [26].

The results obtained are used to explain the appearance of the contour of the ACMSL line, i.e. to establish a regularity of intermolecular interactions of the studied objects.

3 Results

Comparison of the observed regularities of light scattering by liquids under study within the wide range of temperature will make it possible to make conclusions on a character of the thermal motion of liquid molecules and clarify the effect of molecule structure on light scattering and character of inner field in liquids.
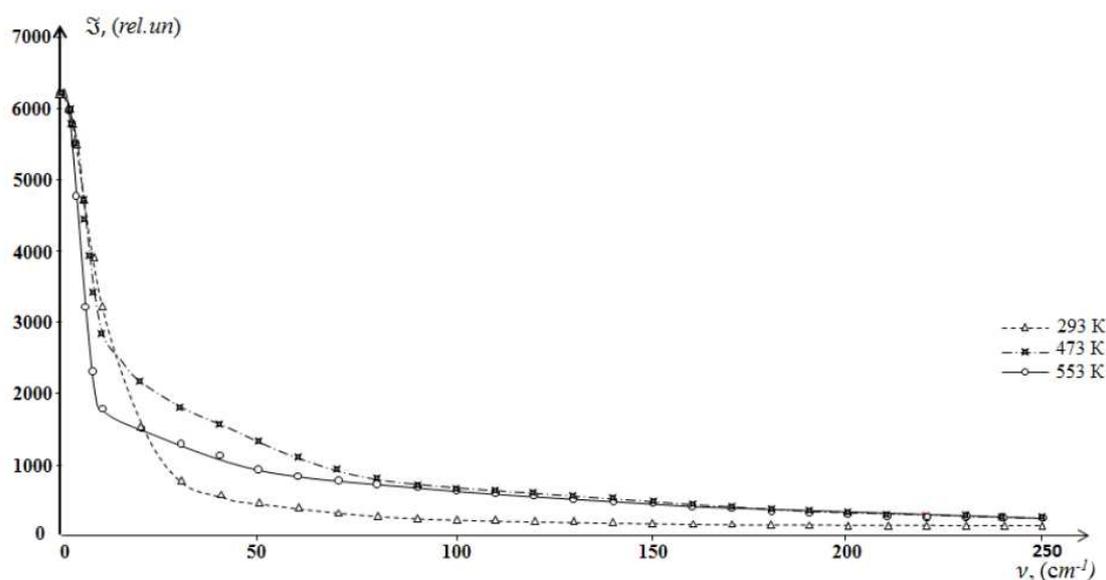

Figure 2: A general view of the ACMSL contour of benzene.

3.1 Benzene

The anisotropic component of molecular scattering of light in benzene was studied within the temperature range 293-553 K.

A general view of the contours of the anisotropic component of scattering depending on temperature is shown in Fig. 2. The curves are normalized to maximal intensity.

As seen from Fig. 2, the half-width of the observed contour becomes wider with the increase in temperature up to $\sim$ 423 K, and a further increase in temperature leads to its narrowing.

The inverse spectral density of the ACMSL contour in benzene as a function of the frequency square for different temperature is shown in Fig. 3.

As seen from Fig.3, within the frequency range $0 \sim 60 \ cm^{-1}$ in the coordinate axes $1/\Im \sim \nu^2$ at room temperature (curve "a") ACMSL consists of two straight lines with different slopes. This is evidence of the fact that the ACMSL contour in benzene within the frequency range $0 \sim 60 \ cm^{-1}$ is a superposition of two Lorentz contours. With heating the liquid, the complexity of the contour remains the same but the inflection point shifts to the low-frequency region (curve "b") and for temperature 553 K the weight of the narrow contour is very small. More probably, at the critical point the complexity of the ACMSL contour disappears.

The results of processing the contour according to the above method are shown in Table 1, where σ_1 , σ_2 are the half-widths of the contour components ("narrow" and "wide"), respectively; α_2 - $(\alpha_1 = 1 - \alpha_2)$ is the weight of the "wide" component.

Table 1.

№	T, K	$\sigma_1, \ cm^{-1}$	$\sigma_2, \ cm^{-1}$	α_2
		C_6H_6		
1	293	2.6	23.8	0.46
2	373	4.0	26.2	0.48
3	423	4.8	17.6	0.56
4	473	3.1	15.0	0.63
5	523	1.6	11.9	0.71
6	533	1.4	11.7	0.71
7	543	1.3	12.1	0.72
8	553	1.2	11.9	0.73
	Statistical error	±0.1	±0.5	±0.02

3.2 Bromobenzene

If benzene (D_{6h} symmetry) is a molecule being axisymmetric in polarizability, then bromobenzene ($C_{2\nu}$ symmetry) is an asymmetric top.

The ACMSL measurements in bromobenzene were carried out within the temperature range 293-623 K and within the spectral range 0-60 cm^{-1}.

The experimental results as the dependence of $1/\Im(\nu)$ on ν^2 are presented in Fig.4. According to this figure, ACMSL in bromobenzene within the frequency range
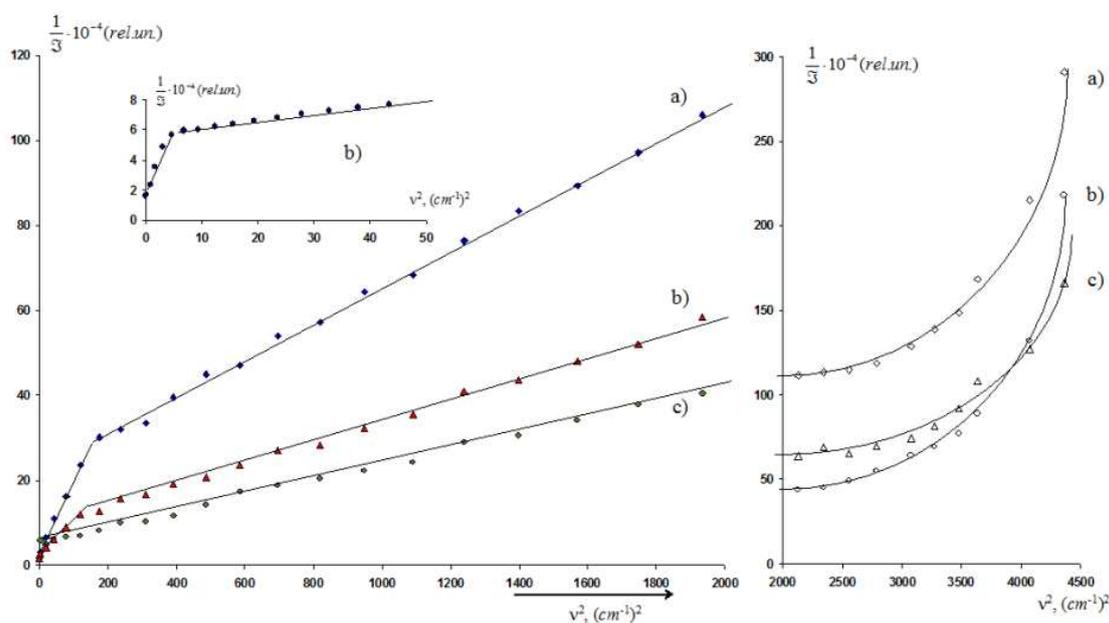
Figure 3: The inverse spectral density of the ACMSL contour in benzene molecule as a function of the frequency square for different temperature: a) 293 K; b) 423 K; c) 553 K.

0-40 cm^{-1} at room temperature (curve "a") consists of two dispersion components with different slopes. This is evidence of the fact that the ACMSL contour in bromobenzene within the frequency range 0-40 cm^{-1} is a superposition of two Lorentz contours. With the raise in temperature the complexity of the contour remains the same but the inflection point shifts to the low-frequency region (curve "b") and for temperature 623 K the narrow contour has the small weight (curve "c").

The temperature behavior of the parameters of the contour components determined as a result of the corresponding processing is shown in Table 2. (The notation is the same as in Table 1, and $\Im_1$ and $\Im_2$ are the spectral intensities at the maximum of the "narrow" and "wide" contours, respectively).

3.3   Aniline and toluene

Aniline $C_6H_5NH_2$ being a nitrogen-containing derivative of benzene and toluene $C_6H_5(CH_3)$ being a radical formed by removing the hydrogen atom from the side methyl group are similar to bromobenzene in symmetry $C_{2\nu}$.

The ACMSL measurements in aniline and toluene were performed within the temperature range 293-623 K.

The results obtained showed that the line contour of molecular scattering of light in the interval of frequency from 0 to 60 cm^{-1} can be approximated with two lorentzians. That is presented in Fig. 5 for aniline and in Fig. 6 for toluene where the two regions of straightening can be clearly seen.

The contour boundary for 293 K is at ~ 20 cm^{-1}. When the temperature increases,
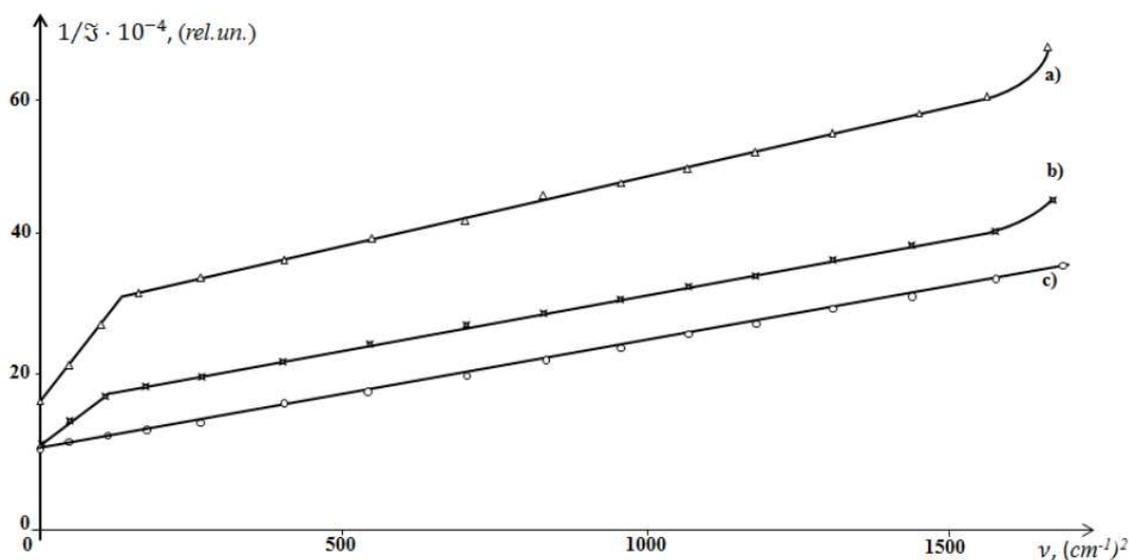
Figure 4: The inverse spectral density of the ACMSL contour in bromobenzene molecule as a function of the frequency square for temperature: a) 293 K ^oC; b) 423 K ^oC; c) 623 ^oC.

Table 2.

T, K	$\Im_1$(rel.un.)	σ_1, cm^{-1}	$\Im_2$(rel.un.)	σ_2, cm^{-1}	α_2
		C_6H_5Br			
293	3200	1.30	40	25.0	0.17
323	3100	1.40	50	22.5	0.20
373	2800	1.45	70	21.0	0.25
423	2700	1.60	125	17.0	0.30
473	2500	1.90	240	11.0	0.37
523	2400	2.20	500	6.30	0.40
573	1100	2.0	600	5.40	0.50
623	1000	1.60	700	3.50	0.60
Statistical error	1-1.5%	±0.1	1-1.5%	±0.5	±0.02

as for the other samples under study, the inflection point shifts to low frequencies. For T=623 K the weight of the narrow contour is less than the wide one.

The parameters of the contour components defined by approximation of the experimental contour with two Lorentz curves within the frequency range 0-60 cm^{-1} are presented in Table 3, where σ_1, σ_2 are the half-widths of the contour components ("narrow" and "wide"), respectively; α_2 - ($\alpha_1 = 1 - \alpha_2$) is the weight of the "wide" component., I is the integral intensity of the contour.

<div style="text-align: right">**Table 3.**</div>

| T, K	$\sigma_1(cm^{-1})$	$\sigma_2(cm^{-1})$	α_2	I(rel.un.)
$C_6H_5NH_2$				
293	0.80	13.0	0.33	34900
373	2.50	13.0	0.40	73500
423	3.40	12.50	0.45	148500
473	3.10	11.80	0.56	157000
523	3.90	12.00	0.62	129400
573	2.50	11.00	0.68	131000
623	1.40	10.00	0.69	121000
Statistical error	±0.1	±1.5	±0.02	6-8%
T, K	$\sigma_1(cm^{-1})$	$\sigma_2(cm^{-1})$	α_2	I(rel.un.)
$C_6H_5(CH_3)$				
293	1.20	10.00	0.33	8000
373	2.50	2.00	0.37	8500
423	2.60	12.50	0.40	8800
473	4.60	12.40	0.46	9000
523	4.60	12.40	0.49	9300
573	3.60	11.00	0.52	8900
623	1.20	10.50	0.56	7800
Statistical error	±0.1	±1.5	±0.02	5-7%
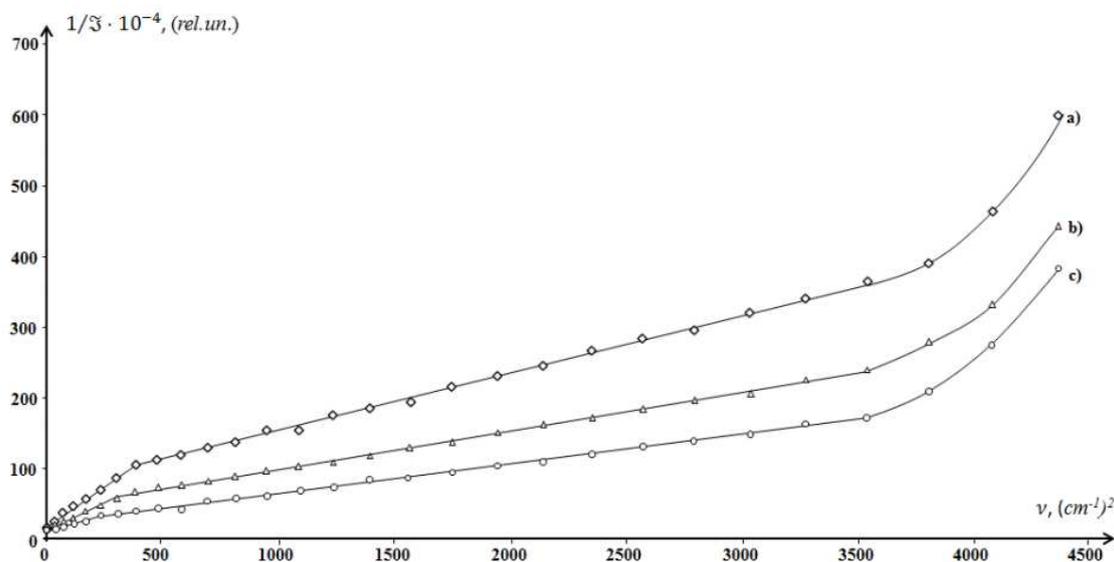
Figure 5: The inverse spectral density of the ACMSL contour in aniline molecule as a function of the frequency square for temperature: a) 293 K; b) 523 K; c) 623K.

3.4 Carbon tetrachloride

In symmetry the carbon tetrachloride molecule CCl_4 is related to a spherical top (T_d symmetry); therefore, anisotropy fluctuations associated with molecule reorientations
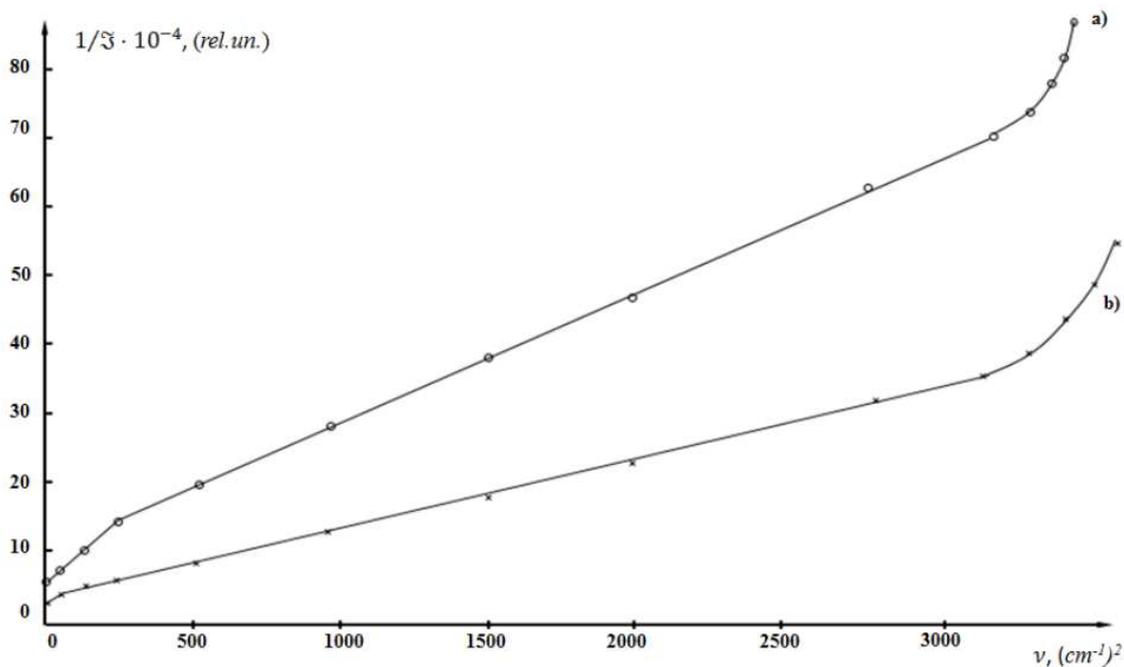
should be optically inactive.

Figure 6: The inverse spectral density of the ACMSL contour in the toluene molecule as a function of the frequency square for temperature: a)293 K; b) 473 K.

The results of graphical representation of the measured contours in the coordinates $1/\Im(\nu)$ of ν^2 for three values of temperature are presented in Fig. 7. The processing of the experimental results by the least squares method is given in Table 4.

Table 4.

T, K	σ_1, cm^{-1}	σ_2, cm^{-1}	$\Im_1$(rel.un.)	$\Im_2$(rel.un.)	α_1	α_2
			CCl_4			
293	2.1	22.2	332	34	0.54	0.46
373	2.4	21.5	301	36	0.53	0.47
423	2.7	21.1	254	38	0.50	0.50
473	3.1	21.5	239	31	0.55	0.45
523	2.3	20.4	261	31	0.53	0.47
543	2.1	22.2	391	34	0.56	0.44
Statistical error	±0.1	±0.1	±1.5	±1.5	±0.02	±0.02

As seen from Fig. 7. (curve "a"), in the region from 0 to $\sim 25\ cm^{-1}$, the observed contour is well approximated by two dispersion contours with an inflection point at $\sim 9\ cm^{-1}$. For temperature close to the critical one (curve "c" in Fig. 8.), there remains practically one contour within this spectral range.
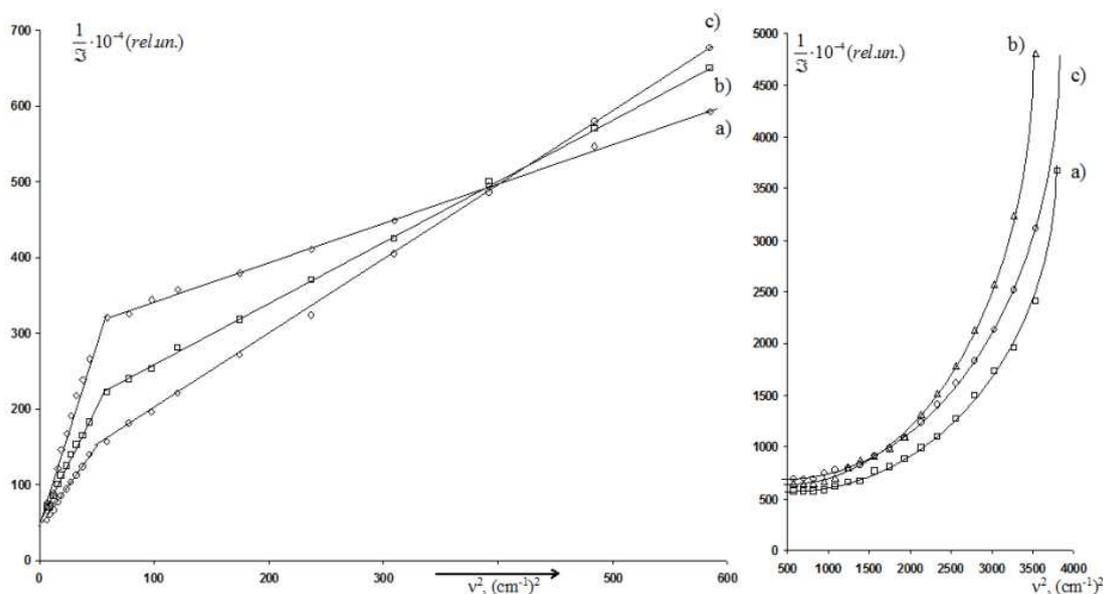
Figure 7: The inverse spectral density of the ACMSL contour in toluene molecule as a function of the frequency square for temperature: a) 293 K; b) 423 K; c) 543 K.

4   Discussion

According to the available data, within the spectral range $0 \sim 50$ cm^{-1}, the ACMSL contour in liquids is a superposition of two dispersion contours – narrow and wide. However, the mechanisms responsible for the origin of the narrow and wide contours differ.

In this work, for all the studied substances at room temperature within the frequency range $0 \sim$ 50-60 cm^{-1}, the observed contour is a superposition of two dispersion contours, narrow and wide, which is in agreement with the available data for these substances [26]-[28]. The whole point is in the interpretation: according to [2]-[29], the narrow contour is associated with reorientations and the wide one with rotational swings (vibrations). We interpret the both components of the contour from the point of view of a model of inhibited rotation of molecules (IRM) of a liquid [26]-[30].

The IRM model is based on the assumption that the molecule rotation is independent relative to three main axes of inertia. Due to the different shape of molecules (different lengths) and due to the anisotropy of the inner field, the rotation inhibition along some axes of inertia will be different. The nature of rotation under strong inhibition should be represented as jump-like turns from one quasi-stable position to another.

If a short-range order exists in a liquid, then for each axis there is not only a well-defined anisotropy, but also, on average, a well-defined field anisotropy. This leads to the fact that each of the 3 rotations corresponds to its own relaxation time and a large difference between their values is possible. The independence of rotation

along three axes leads to the fact that in the anisotropic scattering spectrum there are three dispersion curves with the half-widths $\Delta\nu$ defined by the value "$1/\tau$", where τ is the relaxation time of anisotropy relative to the corresponding axis. In the "gas" approximation the intensity of anisotropic scattering is defined by polarizability anisotropy. Hence, in the total scattering the relative fraction of each component of the contour, or the weight "α_i", should be proportional to the molecule anisotropy in a plane perpendicular to that axis with rotation relative to which the contour is associated. If the axes of polarizability and inertia coincide then

$$\alpha_i = \frac{(a_j - a_k)^2}{(a_i - a_j)^2 + (a_j - a_k)^2 + (a_k - a_i)^2}, \tag{1}$$

(α_i are the main values of the polarizability tensor of a molecule).

The axes choice is shown in Fig. 8.

Specific consequences follow from the IRM model:

1. The contour of the anisotropic scattering line is a sum of three dispersion contours for an asymmetric top and two dispersion contours for a top symmetric in polarizability.

2. It becomes possible to estimate the weights of the contour components "α_i" since the polarizability of free molecules (the gas approximation) is known for all the substances studied in this work. From Figs. 3-7 it is seen that for benzene and its derivatives the complexity of the ACMSL contour remains with the increase in temperature but the inflection point shifts to the low-frequency region.
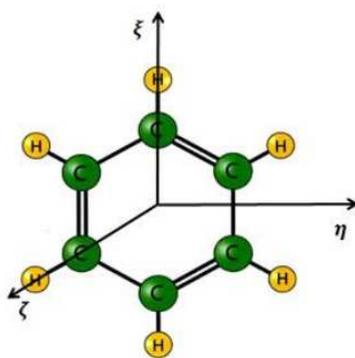
Figure 8

However, when approaching the critical state for almost all liquids under study, in the coordinate axes $1/\Im(\nu)$ and ν^2, the narrow contour is barely visible. The experimentally obtained half-width σ_1 is about 1.1 cm^{-1}, which corresponds to the hardware function of the DFS-12 spectrometer.

It should be noted that, according to the IRM model, in liquids consisting of molecules like asymmetric tops (aniline, bromobenzene) the observed contour should be a sum of three dispersion contours. But, due to the small weight of the third contour, the approximation by two dispersion contour is quite justified.

In the IRM model, the weights of the contour components are generally independent of temperature, because in the model the weight is determined only by the polarizability anisotropy, i.e. the weights are calculated for free molecules in the "gas" approximation. Indeed, the molecule polarizability is a conservative quantity that weakly depends on the state of aggregation and the experimentally observed temperature behavior of the weights (intensities) of the contour components can be caused, first of all, by a change in the correlation of the orientation of liquid molecules [31]. The scattering coefficient R for the anisotropic component in a liquid is as follows

$$R \sim g_{gas}^2 \cdot \gamma, \tag{2}$$

where g_{gas}^2 gas is the optical anisotropy calculated in the gas approximation, γ is the correlation factor

$$\gamma = 1/2(3\cos^2\theta - 1), \tag{3}$$

where θ is the angle between the axes of a pair of the neighboring molecules, γ can vary from 0 (no correlations at all) to $\gamma = 1$ (full ordering).

Changes in the correlations of liquid molecule orientation are not the only factor affecting the temperature behavior of the ACMSL intensity. The point is that the polarizability anisotropy can arise not only due to reorientations, but also due to vibrations.

In the IRM model, the contribution of this mechanism to the weights of the contour components was not taken into account. In a rigorous consideration of anisotropy fluctuations, the contribution of vibrational motion should be taken into account. The point is under what conditions this mechanism has a lot of weight and when it can be neglected. A specific feature of this mechanism is that it leads to faster fluctuations than orientation ones. Consequently, fluctuations associated with vibrational motion should contribute to a wide contour. Vibrational fluctuations have a characteristic time slightly dependent on temperature, but their amplitude increase with temperature (this is the case when a character of the thermal motion of liquid molecules does not change over the entire temperature range of the existence of the liquid state). Moreover, the vibration mechanism leads to the dispersion form of the contour.

A rough estimate of the vibrational mechanism contribution for anisotropic molecules can be made from the gas values α_1^{gas}, α_2^{gas} and α_1 and α_2 calculated from the experiment at the temperature "T" (neglecting the effects of changes in the degree of molecule correlation). Considering, as mentioned above, that the vibrational mechanism contributes only to a wide contour, we can show that the weights of purely rotational and vibrational motion are determined by the following expressions

$$\alpha_{vib} = \frac{\gamma}{1+\gamma}; \ \alpha_{rot} = \frac{1}{1+\gamma}, \ \text{where } \gamma = \frac{1}{\alpha_2^{gas}}(\frac{\alpha_1^{gas}}{\alpha_1^{exp}} - 1). \tag{4}$$

From the data obtained in this work, we will return to them later, it can be seen that with an increase in temperature the contribution of the vibration mechanism for benzene, bromobenzene and aniline is already a large part of the contour.

It is known [31, 32] that at the critical point the correlation radius increases sharply. It can be assumed that the increase in the correlation radius begins long before the critical state. An increase in the correlation radius will lead to the fact that the contribution of vibrational modes to the ACMSL contour should increase and that of rotational ones should decrease. We observe this in our experiment: the half-width of the narrow contour increases with temperature to that close to the boiling point. (In our measurements, the boiling point for all studied liquids is higher than under normal conditions, which is associated with high pressure of saturated vapors). With a further increase in temperature, the narrow contour becomes narrower.

Such a temperature behavior σ_1 can be explained as follows:

With heating and approaching the boiling point, the liquid acquires the properties of a vapor state more and more;

The rotation of the molecules becomes freer and the weights of the contour components should approach the gas values.

With a further increase in temperature, the liquid state is more and more different from gaseous one and at $T = T_{crit}$ the correlation radius tends to infinity. It can be assumed that within this temperature range a character of the thermal motion of liquid molecules changes. As mentioned above, within this temperature range there is a gradual "freezing" of the rotational degrees of freedom because of an increase in intermolecular interaction (an increase in the correlation radius). And the vibrational modes are gaining more weight - increasing the weight α_2 of the wide contour. At a temperature close to critical one, there remains almost one contour associated with vibrational modes.

The experimentally observed fact of reducing the half-widths of the contours at temperatures above the boiling points can be explained for each of the studied liquids. We associate this with a change in the character of the thermal motion of molecules: an increase in the correlation radius, as noted above, leads to "freezing" of rotational degrees of freedom. Hence, there is a gradual transition from a complex contour shape (two dispersion contours) to a simple one (one contour). At the critical point, there must be one contour with the half-width close to that of the hardware function.

On the basis of the above stated the shape and width of the ACMSL contour is analyzed: a symmetric top (D_{6h} symmetry group) in benzene (C_6H_6) and a spherical top (T_d symmetry group) in carbon tetrachloride (CCl_4) [33].

We studied ACMSL in CCl_4 within the temperature range 293-473 K and in the spectral interval 0-70 cm^{-1}, in C_6H_6 within the temperature range 293-553 K and in the spectral interval 0-70 cm^{-1}. In Figs. 3 and 7 we demonstrate some measured ACMSL contours in the coordinates $1/\Im(\nu)$ of ν^2 for three values of temperature for C_6H_6 and CCl_4, respectively.

Visually, the curves for C_6H_6 and CCl_4 look identical: two regions of straightening (each region has its own dispersion contour ACMSL). But for C_6H_6, the inflection is observed at ~ 13 cm^{-1} and for CCl_4 at ~ 9 cm^{-1}. That says that the narrow contour in benzene is longer than in CCl_4.

In Tables 1 and 4, the fact of a weak temperature dependence of σ_1 in CCl_4 in comparison with C_6H_6 is noteworthy. This can be mainly due to the fact that

in CCl_4 the intensity of the anisotropic component of scattering is very small; the integral intensity decreases with increasing temperature and the contribution of the hardware function to the central part increases. Therefore, the main attention we pay to the temperature dependence of the width σ_2 of the wide contour. As seen from Table 4, σ_2 in CCl_4 is almost independent of temperature unlike σ_2 in C_6H_6. If the wide contour is entirely due to the vibration mechanism then, as noted above, the temperature dependence of the width should not be observed. In C_6H_6, the wide contour should be associated with both orientation fluctuations and vibrations. Moreover, with the raise in temperature, the role of the vibration mechanism should increase.

For anisotropic molecules a contribution of the vibrational mechanism can be roughly estimated with the main values of the polarizability components α_i and with the calculated weights of the contour components of ACMSL α_1 and α_2 (α_1 is the weight of the narrow contour, α_2 is the weight of the wide contour).

The calculated values of α_{vib} and α_{rot} for several values of temperature in benzene, bromobenzene and aniline are presented in Table 5.

Table 5.

Benzene							
T, K	α_{gas}^2	α_{gas}^1	α_{exp}^2	α_{exp}^1	γ	α_{vib}	α_{rot}
423	0,5	0,5	0,56	0,44	0,27	0,21	0,79
474	0,5	0,5	0,63	0,37	0,70	0,41	0,59
525	0,5	0,5	0,71	0,29	1,45	0,59	0,41
536	0,5	0,5	0,71	0,29	1,45	0,59	0,41
547	0,5	0,5	0,72	0,28	1,57	0,61	0,39
558	0,5	0,5	0,73	0,27	1,70	0,63	0,37
Bromobenzene							
523	0,33	0,62	0,41	0,59	0,15	0,13	0,87
574	0,33	0,62	0,5	0,5	0,73	0,42	0,58
625	0,33	0,62	0,58	0,42	1,44	0,59	0,41
Aniline							
423	0,41	0,58	0,43	0,57	0,04	0,04	0,96
474	0,41	0,58	0,45	0,55	0,13	0,12	0,88
525	0,41	0,58	0,49	0,51	0,33	0,25	0,75
576	0,41	0,58	0,54	0,46	0,64	0,39	0,61
627	0,41	0,58	0,6	0,4	1,10	0,52	0,48

It can be seen from Table 5 that with the raise in temperature the contribution of the vibration mechanism α_{vib} for benzene and aniline becomes very significant.

It can be assumed that with increasing temperature and approaching the critical state, the ACMSL contour in liquids consisting of anisotropic molecules should be one dispersion curve associated with the vibrational mechanism within the spectral range 0-60 cm^{-1}. The experimental data on the temperature behavior of ACMSL in benzene at T = 553 K (the critical temperature for benzene T = 562.5 K) also support this statement. In Fig. 4 the curve "c" corresponds to temperature of 553 K. It can

be seen that in the coordinates $1/\Im(\nu)$ of ν^2 one straight line is almost observed, i.e. the observed ACMSL contour is fairly well represented by one dispersion contour. The narrow contour has the small half-width σ_1 and small weight α_1. We associate this manifestation of the narrow contour with the hardware function.

These experimental data are direct evidence that near the critical state of a liquid a character of the thermal motion of liquid molecules changes. The rotational degrees of freedom of molecules are "frozen", only the vibrational ones remain, namely the vibrations associated with the cooperative movement of molecules.

Further, the shape and width of the ACMSL contour in bromobenzene (C_6H_5Br) is analyzed over a wide temperature range - from room temperature to almost critical ones. The object is a benzene derivative structurally similar to a benzene-aromatic ring. But one hydrogen atom is replaced by a bromine atom.

First of all, we were interested in the shape of the ACMSL contour because the relaxation processes occurring in the fluid are associated with this shape.

The experimental results are presented in Fig. 4. It is seen from this figure that ACMSL in bromobenzene within the frequency range 0-40 cm^{-1} in the coordinate axes $1/\Im(\nu)$ of ν^2 at room temperature (curve "a") consists of two straight lines with different slopes. This indicates that the ACMSL contour in bromobenzene within the frequency range 0-40 cm^{-1} is a superposition of two Lorentz contours. With heating the liquid, the contour complexity is unchanged, but the inflection point shifts to the low-frequency region (curve "b") and at temperature 623 K (critical temperature 670 K) only one contour remains (curve "c"). A hint of the narrow contour is probably a manifestation of the hardware function.

A technique we developed to decompose the ACMSL contour into components and a liquid IRM model we propose to explain the complexity of the ACMSL contours allowed us to give not only a qualitative picture of the thermal motion of liquid molecules, but also to estimate the weights (contributions) of each of the mechanisms and their temperature changes.

As seen from Table 2, the half-width of the narrow contour monotonically increases with the raise in temperature from 293 to 523 K and the half-width of the wide contour decreases. Such a temperature behavior is in agreement with our model of the IRM liquid. Indeed, we associate the narrow contour with rotation relative to the axes η and ζ. Relative to these axes the molecule rotates with its longest part. Therefore, this rotation is much more inhibited than the rotation about the ξ axis with which the wide contour is associated. In this regard, the temperature more strongly affects the narrow contour and weakly affects the wide one.

However, at temperature T = 573 K and above, an anomaly is observed in the temperature behavior of the half-width of the narrow contour: the contour narrows; for the wide contour the rate of half-width changes within this temperature range increases as compared to the behavior for lower temperatures.

In addition, according to the IRM model, the weights of the contour components calculated in the gas approximation (based on the main values of free molecule polarizabilities) should approach the theoretical values for temperatures close to critical, since the critical state in physics is usually considered as a state close to gaseous one.

However, our experimental results do not agree with this point of view. For example, the experimentally found weight of the wide contour α_2 is close to α_2^{theor} at T = 423 K and it significantly increases at higher temperatures. All these anomalies do not fit into the framework of the IRM model. More probably, at temperatures above 423 K a character of the thermal motion of liquid molecules changes.

With heating, the liquid state becomes nonequilibrium. As the liquid temperature approaches the critical one, a degree of nonequilibrium increases greatly. It is known that in the nonequilibrium state the collective degrees of freedom begin to manifest themselves [34]. Moreover, the greater the disequilibrium is, the greater the influence of collective degrees (collective modes) is. Near the critical state, the collective modes are likely to dominate. Therefore, a decrease in the half-width of the observed ACMSL contour in bromobenzene can be associated precisely with the restructuring of the liquid structure (the increasing influence of the collective degrees of freedom).

At T = 523 K, an additional mechanism of the appearance of anisotropy fluctuations is activated, the collective modes appear. First of all, the collective modes should affect the low-frequency contour, which is observed (column 3 in Table 2). At T = 573 K, an anomaly is observed in the half-width of the narrow contour – a narrowing begins with increasing temperature. The temperature shifts existing between the sharp narrowing of the wide contour (σ_2) and the anomaly of the narrow one can be probably explained by different weight ratios between the mechanism of the IRM model and the collective modes. Near the critical state, the mechanism of the IRM model probably no longer works, and everything is determined by the collective modes. From that we can understand the fact that the complexity of the ACMSL contour at high temperatures disappears, i.e. the contour shape undergoes further simplification (Fig. 4, curve "c"). With increasing temperature, the weights of the component contours of the ACMSL can change due to changes in the correlations of the molecular orientation.

The presence of the temperature behavior of the weights of the Lorentz components indicates that the contour weight in liquid is determined not only by the anisotropy of the polarizability tensor, but also by the correlation of liquid molecule orientation. With increasing temperature, the weights of the ACMSL contour components can change due to changes in the correlations of the molecular orientation. The scattering coefficient R for ACMSL in liquid, calculated in the gas approximation, can vary from 0 (complete absence of correlation) to 1 (complete ordering).

A change in the correlation of the orientation of the liquid molecules is not the only factor affecting the temperature behavior of ACMSL. The point is that polarizability anisotropy can arise not only due to reorientations of molecules, but also due to vibrations. Calculations of the weights of the contour components in the IRM model do not take the contribution of this mechanism into account. In a rigorous consideration of the occurrence of anisotropy fluctuations, this contribution should be taken into account.

We present the experimental results for toluene and aniline liquids whose molecules have the same $C_{2\nu}$ symmetry and one base (benzene ring), but differ in bonds.

Since the weight of the third contour α_3 calculated with formula (1) is very small

(2-4for both substances then the observed scattering profile of each liquid can be represented by a sum of two dispersion contours (narrow and wide); the contour associated with rotation relative to the axes μ and ζ will be narrow. The axes for the toluene molecule are shown in Fig. 9.
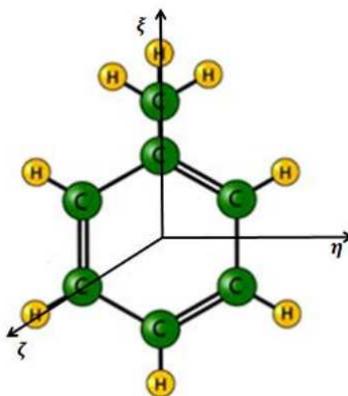

Figure 9

The fact is that the half-widths of the contour components (σ_i) are determined by the characteristic times of jump-like transitions from one quasi stationary state to another. Relative to the axes μ and ζ the aniline and toluene molecules rotate with their longest part. Therefore, these rotations will be most inhibited; hence the anisotropy relaxation time along these axes will be longer than that along the ξ axis. The wide contour is associated with rotation about the ξ axis – the axis of light rotation.

The studies showed that the observed contour of the ACMSL line for toluene and aniline (in the coordinates $1/\Im$ of ν^2 where I is the spectral density of the ACMSL line contour) is a sum of two dispersion components within the range from 0 to 60 cm^{-1} at room temperature. With heating the liquid, the inflection boundary moves to low frequencies (Fig. 5 and Fig. 6).

The results of processing the experimental contours of the dispersion components (α_1 , α_2 and σ_1 , σ_2 obtained by decomposition of the experimental contour into components by the method of successive approximations are presented in Table 3.

The regularities of the temperature behavior of the parameters of the contour components for both substances are of the same nature. The narrow contour (σ_1) has a sharp temperature dependence; the half-width of the wide contour (σ_2) depends weakly on temperature. This temperature behavior of the half-width can be naturally explained in the framework of the IRM: the narrow contour is associated with the rotation of the most difficult turning relative to the axes μ and ζ (lying in the ring plane). Therefore, it is natural to expect that with the raise in temperature (when the liquid is heated) the movement be defrosted along these axes. The half-width of the wide contour associated with rotation relative to the ζ axis (passing through the carbon vertices of the ring) – the axis of light rotation – weakly depends on temperature due to almost free rotation. Accordingly, the half-widths of the contour

components of the anisotropy relaxation time along the axes μ, ζ, and along the axis ξ will be very different.

Consider the weight values and their temperature behavior. When the liquid is heated, a decrease in the intensity of the narrow contour (intensity in the center) and an increase in the intensity of the wide contour (peripheral areas) are observed. A comparison of the theoretical and experimental values of the weight of the contour components shows that at room temperature the weights α_1 and α_2 for both substances differ from α_1^{theor} and $\alpha_2^{theor} + \alpha_3^{theor}$. With the raise in temperature, the discrepancy decreases; at temperature 373 K the calculated α_1^{theor} and the experimental values α_1 almost coincide; a further increase in temperature again leads to a discrepancy. This may be due to the fact that in the scattering process not only rotational motion is observed, but also other types of it, in particular, vibrational motion [2]. It should be noted that there is no single point of view on the nature of the wings of the ACMSL contour. In [29], the narrow contour is associated with orientation fluctuations, and the wide one with vibrational motion. We associate the discrepancy between the values of α^{theor} and those obtained experimentally for high temperatures of substance with the contribution of the vibrational mechanism to ACMSL. This mechanism will contribute to the peripheral parts of the contour, since the characteristic time of vibrational motion is not less than the characteristic time of inhibited rotation and the weight of the vibrational mechanism increases with the raise in temperature.

With the data of Table 3 for 473 K we obtain $\alpha_{vib} = 0.49$ for toluene and $\alpha_{vib} = 0.44$ for aniline, i.e. slightly less than half of the wide contour is associated with the vibration mechanism.

There is one more experimental indication that when the liquid temperature approaches the critical one, a new mechanism begins to take part in ACMSL. The point is that the approximation of the ACMSL contour in toluene and aniline by two dispersion contours at room temperature is good. With the raise in temperature, a degree of the approximation becomes worse, and mainly in the peripheral areas. This fact indicates that the contribution of the vibration mechanism at low temperatures is still small.

Our studies of the temperature-frequency behavior of the ACMSL spectrum are evidence of manifestation of the processes associated with structural rearrangements of liquid.

Our proposed model of inhibited rotation of molecules in a liquid well explains the experimentally observed regularities both in the number of contours and in the temperature behavior of the parameters of the contour components for objects with regularly changing molecular structures.

Different authors associate the ACMSL contour with the processes such as Brownian rotational motion, inhibited rotation, vibration, shift deformation, etc. Certainly, all these mechanisms contribute to the ACMSL spectra and the task is to establish the main mechanisms under specific experimental conditions.

5   Conclusion

An original series of the complex experimental studies was performed on the MSL Raman spectra for a number of practically important organic liquids - hydrocarbons and their halogen-substituted ones within the frequency range 0-200 cm^{-1} ; they are devoted to developing the scientific basis for the application of a method of fluctuation of the local field of the light wave; this method establishes the relationship between the experimentally observed spectra of light scattering and the corresponding regularities of the intermolecular interaction in condensed matter.

It can be concluded that the distribution of the ACMSL intensity in a substance within the indicated frequency range (0-60 cm^{-1}) is described by two contour components: "narrow" one arising due to the reorientation of the vibrational mechanism of molecular motion and "wide" one due to the movement of molecules in a potential well. With the raise in temperature and liquid approaching a critical state, the frequency range of the transition from the central lorentzian to gaussian shifts to high frequencies, which is another confirmation in favor of a hypothesis of the origin of the high-frequency region of the spectrum owing to dephasing. From the shape of the high-frequency wing of the MSL anisotropic component line in a liquid, it is possible to obtain information on the fundamental phenomenon of statistical physics - phase mixing that we will study in our further research. Reference

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